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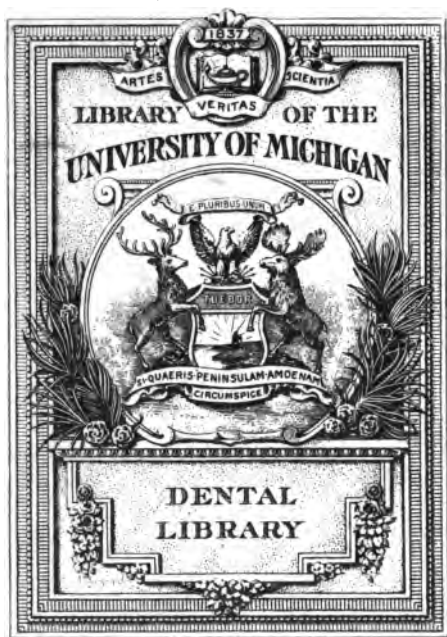
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DENTAL METALLURGY.

FOR THE USE OF DENTAL STUDENTS
AND PRACTITIONERS



BY

EWING PAUL BRADY, D.D.S.

PROFESSOR OF CHEMISTRY, PHYSICS, METALLURGY, MATERIA MEDICA, THERAPEUTICS AND SPECIAL PATHOLOGY, WASHINGTON UNIVERSITY
DENTAL SCHOOL, ST. LOUIS, MISSOURI

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PREFACE.

IN this manual on the subject of dental metallurgy I have endeavored to emphasize those properties of the various metallic elements which are of particular interest to the dentist.

As in every other science, there are branches which border on kindred sciences. Such operations as involve prosthesis are treated only in such detail as to emphasize the metallurgical principle involved.

The chemical properties of the metals are dealt with very superficially, as this knowledge should have been acquired by the student before any attempt is made to study metallurgy.

The chemical test for the metals, both in the dry and wet way, is placed in the back of the book. The object of this is twofold: in the first place it tends to condense the chapters on the individual metals, and secondly, the theme of analysis may be used in the study of qualitative analysis, and being condensed in one chapter is in more convenient form.

The course in metallurgy, as I have been conducting it for a number of years, is given at the same time as the course on qualitative analysis. The advantage of such an arrangement is that the chemical properties of the metals are thoroughly studied in conjunction with metallurgy, in which the physical properties are of the greatest importance.

In the preparation of this volume I have made frequent references to the following valuable works on Metallurgy: Fenchel, Schnabel, and Essig and Koenig; on Chemistry: Oswald, Newth, Smith, and Remsen; Qualitative Analysis: Prescott and Johnson; Mineralogy: Moses and Parson, and Dana; Prosthetic Dentistry: Prothero; Assaying: Brown; Physics: Ganot; and the various scientific journals.

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E. P. B.

ST. LOUIS, 1917.

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DENTAL METALLURGY.

CHAPTER I.

METALLURGY.

Historical.—The history of prehistoric ages depends upon relics for the study of the people living in the remote past. Depending upon the nature of these relics, it is possible to determine the state of civilization, habits and also peculiarities of the race under consideration. The lower savages of the present day correspond to the oldest traces of man. In order to leave traces, it was necessary for primitive man to make something, not subject to quick decay or easily destroyed.

The age known as the "paleolithic" or "old stone age" is designated as that period in which man had advanced to that degree, which enabled him to work rocks into some useful form so as to serve in his daily life. Arrow-heads and various other flint implements, in their crudest form, are among the relics found corresponding to this age. The "neolithic," "new stone age," following this era, shows culture has advanced, and the stone implements in this period assume a higher degree of workmanship.

The "neolithic" period varied in length of time in different localities; however, long ages must have passed before metals were made use of by mankind. Copper in its native state (too soft to be of material value to primitive man), when hardened by the admixture of tin, forming bronze, was brought into use later. That this occurred in countries beyond the Mediterranean, before any people in Europe found the metals secreted in their ores, appears to be more

than probable, and formerly it was assumed that the use of copper and bronze, followed later by the use of iron, came into Europe from the East. Now there is a growing opinion that primitive metallurgy in some parts of Europe was an art independently acquired.¹ The more advanced of the native races were acquainted with copper and bronze, tin, lead, gold, and silver.

Sacred history teaches us that the metals were made use of at a very early age. One of Adam's grandsons was a worker in metals and frequent mention of gold, silver, bronze, etc., is made in the Bible.

The development of chemical science has been divided into several stages, and as the early history of metallurgy is identical with that of chemistry, it may be permissible to quote the history of the two sciences as if they were one and the same.

1. **Ignorant Observation.**—In this period experimentation was carried on in a haphazard manner, as no set laws had been formulated. The observer was simply following, as we may say, his own initiative. Rarely were records kept, and humanity or science was rarely benefited as the result of the efforts expended.

2. **Isolated Observation.**—This period is so called because the investigators guarded very zealously their efforts: and, as a rule, worked in hidden places, and science was not benefited, due to the fact that there was no coöperation between the investigators of this period.

Alchemy, with its prime object to find the philosopher's stone, may be classed in this period; and one may indeed excuse this set of men, when we consider the object of their endeavors was to find a substance which would change base metals into gold or silver. Their laboratories were sacred to them, no one was permitted to view their operations; mystic signs were used, and their favorite deity called upon to assist in their work. Up to this period the chief impetus to the development of chemistry was through the metallic

¹ Larned.

elements, and without a doubt this period may be considered the forerunner of the development of our present-day science of metallurgy.

The phylogiston theory was the common belief of the alchemists; according to this theory a substance undergoing rapid oxidation or combustion burned, losing phylogiston. Combustible substances possessed phylogiston, non-combustible substances did not. This peculiar substance when combined with other substances made them weigh less, after burning, which was described as the act of a substance losing its phylogiston, the calx or ash resulting weighed more or possessed the original weight of the substance devoid of phylogiston.

The elements were four, namely, earth, warm and moist; water, cold and moist; air, cold and dry; fire, hot and dry. With these four elements and the phylogiston theory, attempts were made to explain the various phenomena that were met with.

3. True Scientific Investigation.—We may date this period with the introduction of the chemical balance by Lavoisier and the thorough understanding of the chemical phenomenon of oxidation about the year 1776. From this time we have the setting aside of the older theories such as have been mentioned, and the introduction by degrees of our present-day views upon the science of chemistry.

One factor which has done more to further the progress of science than any other fact which may be brought to bear is that of coöperation of the investigators. By the combined efforts and setting of professional narrow-mindedness we have all gained knowledge from one another.

It may be readily seen by reviewing the past that metallurgy has played its part in the rise of mankind from the primitive. As industry increased the needs for metals and alloys has increased correspondingly, and one has only to look to our own profession to see that at the present time there is a crying need for advancement and research investigation to provide for emergencies which have developed in the metallurgical side of dentistry.

CHAPTER II.

METALS.

METALLURGY is a very extensive science and, like others, must depend upon its kindred sciences for its development. Geology, mineralogy, physics and chemistry, all have a direct bearing upon this science. A knowledge of chemistry and physics is absolutely necessary for the proper understanding of metallurgy.

Metallurgy may be defined as the science which treats of the physical and chemical properties, mode of occurrence, reduction from their ores, and application to useful purposes of the metallic elements.

Chemistry teaches us that the universe is made up of matter and energy. Matter being composed of simple substances called elements, and also a combination of these elements known as chemical compounds. The number of elements is constantly subject to change, and at the present time there are about eighty substances classed as elements. These are again divided into metals and non-metals. The names of the metallic elements and their principal valency so far known with certainty are as follows:

INTERNATIONAL ATOMIC WEIGHTS. 0 = 16. 1913.

	Symbol.	Valency.	At. Wt.
Aluminum	Al	III	27.1
Antimony	Sb	III or V	120.2
Arsenic ¹	As	III or V	74.96
Barium	Ba	II	137.37
Bismuth	Bi	III or V	208.0
Cadmium	Cd	II	112.4
Caesium	Cs	I	132.81
Calcium	Ca	II	40.07
Cerium	Ce	III or IV	140.25

¹ Metalloid.

INTERNATIONAL ATOMIC WEIGHTS. 0 = 16. 1913.—(Continued.)

	Symbol.	Valency.	At. Wt.
Chromium	Cr	II or III	52.0
Cobalt	Co	II or III	58.97
Copper	Cu	I or II	63.57
Erbium	Er	III	167.7
Gadolinium	Gd	III	157.3
Gallium	Ga	III	69.9
Germanium	Ge	II or IV	72.5
Gold	Au	I or III	197.2
Indium	In	III	114.8
Iridium	Ir	II, III or IV	193.1
Iron	Fe	II or III	55.84
Lanthanum	La	III	139.0
Lead	Pb	II or IV	207.1
Lithium	Li	I	6.94
Magnesium	Mg	II	24.32
Manganese	Mn	II, III or IV	54.93
Mercury	Hg	I or II	200.6
Molybdenum	Mo	II, III, IV or V	96.0
Nickel	Ni	II or III	58.68
Niobium	Nb	III or IV	94.0
Osmium	Os	II or IV	190.9
Palladium	Pd	II or IV	106.7
Platinum	Pt	II or IV	195.2
Potassium	K	I	39.1
Radium	Ra	II	226.4
Rhodium	Rh	III	102.9
Rubidium	Rb	I	85.45
Ruthenium	Ru	II, III or IV	101.7
Samarium	Sm	III	150.4
Scandium	Sc	III	44.1
Selenium ¹	Se	II or IV	79.2
Silver	Ag	I	107.88
Sodium	Na	I	23.0
Strontium	Sr	II	87.63
Tantalum	Ta	V	181.5
Tellurium	Te	II or VI	127.5
Terbium	Tr	III	159.2
Thallium	Tl	I or III	204.0
Thorium	Th	III or IV	232.4
Tin	Sn	II or IV	119.0
Titanium	Ti	IV	48.1
Tungsten	W	II, IV, V or VI	184.0
Uranium	U	III, IV, V or VIII	237.0
Vanadium	V	II or IV	51.0
Ytterbium	Yb	III	172.0
Yttrium	Y	III	89.0
Zinc	Zn	II	65.3
Zirconium	Zr	IV	90.67

Considered a non-metal.

The metals vary in their degree of usefulness; some are met with in every-day life, while others are mere curiosities.

The following seventeen metals are used to a greater or less extent in the metallic condition. These are:

Antimony,
Aluminum,
Bismuth,
Copper,
Gold,
Iridium,
Iron,
Lead,
Manganese,

Mercury,
Nickel,
Platinum,
Tantalum,
Tungsten,
Silver,
Tin,
Zinc.

For dental purposes, the following metals are of the most importance, namely:

Antimony,
Aluminum,
Bismuth,
Copper,
Gold,
Iridium,
Iron,
Lead,

Mercury,
Nickel,
Platinum,
Silver,
Tin,
Tantalum,
Tungsten,
Zinc.

Eighteen are more or less extensively used in medicine and in the arts as coloring pigments and for alloying purposes. These are:

Antimony,
Arsenic,
Barium,
Bismuth,
Cadmium,
Calcium,
Chromium,
Cobalt,
Copper,

Lithium,
Manganese,
Mercury,
Potassium,
Sodium,
Tungsten,
Titanium,
Uranium,
Zinc.

The remaining metals are of very little or no practical use in the metallic state.

The metallurgist classifies the metals into two classes—the noble and base metals. A noble metal is one that forms unstable oxides, and is reduced from their oxides by simply

heating to redness. Base metals, on the other hand, form stable oxides, and it requires the presence of certain substances, known as "reducing agents," before they may be freed from combination with oxygen, when heated to redness. The noble metals consist of the platinum group, together with gold, silver, and mercury.

	Symbols.	At. Wt.
Platinum group	Platinum	Pt 195.2
	Osmium	Os 190.9
	Iridium	Ir 193.1
	Palladium	Pd 106.7
	Rhodium	Rh 102.95
	Ruthenium	Ru 101.7
Gold	Au	197.2
Silver	Ag	107.88
Mercury	Hg	200.6

The elements are also classified into families or groups, according to their atomic weights; this forms a basis for the "periodic classification" or the so-called "law of Octavos." According to this classification we have the "alkali metals" (sodium, potassium, lithium, etc.); "alkali earth metals" (calcium, barium, strontium, etc.); zinc, copper, aluminum, iron, tin, antimony and gold-platinum groups.

Finally, metals may be classified according to their behavior in solution toward certain reagents, as in the five or six groups of qualitative analysis. We mention the various ways in which the metals may be classified to show how indefinite the question often asked, "How are metals classified?" seems to a person who has made a study of this subject.

The metals occur in nature widely distributed, and may be found in the metallic condition, "native state," in combination and as impurities in other metallic substances.

The native metals generally contain admixtures of other metals—rarely are they found in the pure condition. The natural occurring compounds of the metals are known as minerals. A mineral may be defined as "a natural occurring compound of a metal formed by inorganic nature, generally possessing a definite crystalline form." The native metals

and also minerals are often associated with earthy impurities. These impurities are known as gangue, vein-stuff, or chat.

An ore is a material containing one or more metals in the free or combined state. This term is generally restricted to a material bearing some metal in paying quantities. The difference between an ore and a mineral is that the latter is a chemical compound, while the former may be composed of two or more minerals or the elementary metal as a complex mixture.

The third source of metals which in some instances is very important is the presence of a metal in an ore in which some other metal predominates. Gold as an impurity in iron and lead ores, silver in lead ore, and cadmium in zinc ores, illustrates this mode of occurrence.

It has been estimated that 99 per cent. of the earth's crust consists of nine elements in the following proportions:

Oxygen	49.98	Calcium	3.51
Silicon	25.30	Magnesium	2.50
Aluminum	7.26	Sodium	2.28
Iron	5.08	Potassium	2.23
		Hydrogen	0.94

Practically none of these exist in the free state, but combined for the most part as silicates and oxides and, with rarer elements, as carbonates, haloids, and sulphates. The unoxidized substances, such as sulphides, are comparatively rare.

Identification of Metals in their Ores.—The physical properties of the mineral is examined, such as the crystal form, hardness, and lines of cleavage. A blow-pipe analysis is next made; this consists of bead tests, charcoal block reactions, and flame tests. The wet methods of qualitative analysis is generally used to confirm the findings of the blow-pipe. As a rule the dry methods of analysis is used by the prospector, and are sometimes spoken of as field tests, because they are made at the site where the ore is discovered. The chemical laboratory is an absolute necessity for the performance of the wet tests.

Quantitative Methods.—These are also classified into wet and dry methods.

Assaying is that science which enables us to find out of what a substance is composed, and the proportions, by means of dry reagents and heat.

The wet methods are divided into two classes:

(a) Volumetric analysis, using solutions of definite strength, known as standard or normal solutions.

(b) Gravimetric analysis, precipitating the element and calculating the quantity present from the weighed precipitate.

LINDHARD (PATENTED) KOMMUTER.

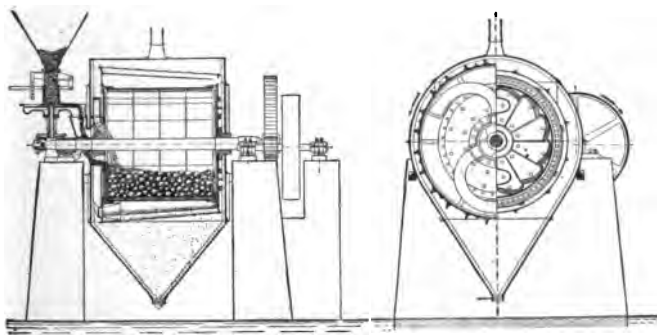


FIG. 1

Treatment of Ores.—The ore is crushed to reduce it to a suitable size. A ball-mill may be used, or some other form of machine which accomplishes the same purpose. The ball-mill (Fig. 1) consists of an iron drum which is caused to revolve. On the inner side there are step-like projections, and iron balls; in some cases Iceland pebbles are placed inside the drum, and when the drum revolves the pebbles or balls crush the ore against the projections. The ground ore sifts through screens located between each projection and is collected below the mill.

The next treatment is to concentrate the ore, and for this purpose the crushed ore is treated with water and run over

gravity tables (gig tables), the earthy material of less specific gravity passes to one side, and the heavier metal-bearing ore to another side of the table. The concentrates are then subjected to some of the following processes in order to further remove impurities or aid in the reduction.

Calcination.—The object of this process is to remove organic impurities and water; by heating to a low red heat it renders the ore more porous.

Roasting.—Roasting consists in heating to a higher temperature, expelling substances which can be volatilized, such as arsenic, sulphur, carbon dioxide, etc. The metals, as a rule, are reduced to their oxides as the result of this process.

Sublimation.—Sublimation is the process of heating a substance until it volatilizes and the vapor is collected as a solid. Arsenic, arsenious oxide, ammonium chloride are substances which may be sublimed.

Distillation.—Distillation is a similar process of boiling, but the vapor collects as a liquid. Mercury, zinc, cadmium may be distilled.

Smelting.—Smelting is a process of refining a metal-bearing substance by fusing. It is necessary at times to remove foreign material present in an ore by chemical means. During the smelting process these materials become oxidized, and the nature of these oxides determine the material which must be added to remove them. If the oxides are of an acid nature, such as silica, it will be necessary to add a substance of a basic nature, such as lime-stone. At the temperature of the furnace, the calcium oxide formed combines with the silica, forming calcium silicate.



The calcium silicate is a fusible glass, and rises to the top of the crucible, and is spoken of as a fusible slag. If, on the other hand, the impurities present are basic oxides, then an acid material like silica or the silicates are added.

A substance which possesses the property of combining with the impurities present in an ore, thus forming a fusible

slag, is called a *flux*. There are two varieties of fluxes: acid and basic fluxes.

In soldering we use a flux, the object being to remove any oxide which may be formed, due to the heating of the metallic surface. (See Soldering.)

Lixiviation.—Lixiviation is a process of washing an ore to remove soluble compounds. Low-grade copper ores are roasted with sodium chloride, then washed or lixiviated, and the soluble copper chloride is recovered from the water by a precipitation method.

Desiccation.—Desiccation is simply heating an ore to a temperature slightly above the boiling point of water in order to dry the ore.

Regulus.—Regulus is a term applied to certain sulphides formed during the process of smelting in the presence of sulphur. Iron, copper, or silver ores when smelted in the presence of sulphur form a regulus. Speiss is the arsenides of certain metals formed during fusion, while Matte is a term embracing both of these and includes sulphides, arsenides, and antimonides of the metals formed during fusion.

CHAPTER III.

PROPERTIES OF THE METALS.

A METAL may be defined as an elementary substance, usually solid at ordinary temperature (except mercury, a solid below -39.44° C.), crystalline in nature, insoluble in water, fusible by heat, and possessing a peculiar luster, commonly spoken of as "metallic luster."

To these qualities must be added those of conducting heat and electricity which the metals possess to the greatest extent, and the power of the metals, with a few exceptions, of replacing the hydrogen of an acid. They form basic oxides with oxygen and finally give off positive ions in solution.

Such substances as arsenic and selenium lie on the borderline between metals and non-metals. Arsenic is sometimes called a metalloid, while selenium is, as a rule, placed in the sulphur group of non-metals.

Fusibility.—There is a great range in the fusing points of the metals (mercury fusing at the temperature of -39.44° C.), and at the other extremes we have certain members of the platinum group that require the greatest heat to fuse. The following is a list of fusing points of metals:

METALS FUSING BELOW INCIPIENT RED HEAT (525° C.).

	Centigrade	Fahrenheit.
Mercury	-39.44	-38.55
Potassium	$+62.5$	$+80.5$
Sodium	95.6	140.0
Lithium	180.0	356.0
Tin	232.0	450.0
Bismuth	270.0	518.0
Cadmium	320.0	608.0
Lead	326.0	618.0
Zinc	415.0	779.0
Antimony	425.0	797.0
Arsenic volatilizes before fusing	450.0	841.0
Tellurium	452.0	845.0

METALS FUSING AT RED HEAT (FROM 700° TO 900° C.).

	Centigrade.	Fahrenheit.
Aluminum	654.5	1230.0
Magnesium	800.0	1472.0

METALS FUSING ABOVE RED HEAT.

	Centigrade.	Fahrenheit.
Silver	960.0	1760.0
Gold	1120.0	2012.0
Copper	1200.0	2192.0

METALS FUSING AT HIGHEST HEAT OF FORGE, OR ABOVE WHITE HEAT (1300° C.).

	Centigrade.	Fahrenheit.
Manganese	1242.0	2268.0
Cast iron	1250.0 to 1300.0	2300.0 to 2350.0
Pure iron	1600.0 to 1804.0	2913.0 to 3400.0
Nickel	1450.0	2632.0
Cobalt	1500.0	2732.0
Palladium	1500.0	2732.0
Platinum	1753.0	3200.0
Rhodium	1946.0	3524.0
Ruthenium	(less than Osmium)	
Tantalum	2770.0	5018.0
Iridium	2300.0	4172.0
Osmium	2500.0	4532.0
Chromium	2000.0	3632.0
Tungsten	3100.0	5600.0

The fusing points of metals above red heat must be considered only approximately, as the physical condition of the metal, and also the method made use of, in determining these temperatures, have a great influence upon the figures arrived at to represent their melting point.

Incipient red heat is generally considered about 525° C.; dull red, about 700° C.; cherry red, 900° C.; deep orange, 1100° C.; white, 1300° C.; dazzling white, 1500° C.

Boiling Points.—As a rule very little is known of the metals in the state of vapor. The boiling points are so high that it is impossible to observe the nature of the vapor, as we do not possess a substance which can withstand these extremes of temperature and at the same time be transparent.

Some of the more readily volatilized metals are: zinc, cadmium, mercury, arsenic, tellurium, potassium and sodium;

while a few others impart a characteristic color to the flame when heated and are probably volatile to a limited extent.

Under ordinary temperatures of the blow-pipe some of the metals do not appear to become volatile, and these are called "fixed" metals. Gold, copper, nickel, etc., belong to this class.

Gold volatilizes when it contains other metals, but in the pure state it requires an extremely high temperature. Gold containing admixtures of copper, lead, or silver, volatilizes at a temperature slightly above the fusing point of the alloy.

The following is a list of a few metals whose point of volatilization has been determined:

Lead	327° C.	Aluminum	1800° C.
Mercury	357°	Manganese	1900°
Cadmium	756°	Silver	1955°
Zinc	916°	Chromium	2200°
Magnesium	1120°	Tin	2270°
Bismuth	1420°	Copper	2310°
Antimony	1440°	Iron	2450°
Gold	2200°		

(H. C. Greenwood.)

Metallic Luster.—All metals possess this property, and their opacity in all probability causes the reflection of the light rays from their surfaces, the effects of which is to produce a luster. Metallic surfaces not only cause the refraction of light but also of heat. This is taken advantage of in the construction of heating devices. Furnaces have been constructed, consisting of metallic mirrors in which heat waves are allowed to be reflected from their surfaces. These mirrors are concave in shape and the heat waves are focussed upon a common point, and in this manner a great concentration of heat is obtained.

The reflecting power of a substance is its property of throwing off a greater or less proportion of the heat reaching a surface, and is measured by the ratio of heat reflected to the incident quantity, or the heat reflected, divided by the quantity of heat received by the surface. The following is a list of the reflecting powers of some metallic substances:

Polished brass	100
Silver	90
Steel	70
Lead	60
Glass	10

This power of substances of reflection is of great importance in the operation of soldering. When an investment material is used it frequently happens that a metallic piece may be ruined by the action of the reflected heat from the surfaces of the investing material.

Conductivity of Heat.—The metals are the best conductors of heat but they vary with each other; some possessing this property to a remarkable extent. There are two methods of determining the conductivity: in one method the rise in temperature of various metals is compared by the use of a thermometer, and then a comparison is made, using the conductivity of silver as 1000. The following is a list of conductivities as determined by this method:

Silver	1000	Steel	116
Copper	736	Lead	85
Gold	532	Platinum	84
Brass	231	German silver	63
Zinc	190	Bismuth	18
Tin	145	Mercury	13
Iron	120	(Wiederman and Franz).	

The figures determined by this method are only approximate. A much more accurate method of determining this physical property of metals is by determining the quantity of heat which is conducted by a metal in a given unit of time. The following figures are the result of determination in which the number of calories of heat which are conducted by the various metals in a second of time are used as the standard, silver being taken as 100:

Silver	100.0	Tin	13.7
Copper	94.6	Platinum	10.4
Gold	66.5	Lead	7.3
Aluminum	31.1	Antimony	4.0
Zinc	27.5	Bismuth	1.8
Iron	14.4	Mercury	1.8

The thermal conductivity of the metals is of some importance to the dentist, as it must be taken into consideration in various operations about the mouth. Metallic fillings being good conductors of heat, convey the various changes of temperature occurring in the mouth more readily than tooth substance and as a result thermal insults are conveyed to the dental pulp and may result in the production of inflammatory changes in this organ. Prosthetic substitutes are subject to the same conditions: gold used as a base for artificial dentures will convey the thermal changes more readily to the mucous membranes than vulcanite, as may be seen by a comparison of their thermal conductivities: gold being represented by the figures 66.5 and ebonite (vulcanite) 0.034.

Expansion by Heat.—When metals are heated they expand, and this property varies with the metal under consideration. Each metal possesses its own degree of expansibility. This may be represented by measuring the amount of expansion in one direction—linear expansion; in two directions, superficial expansion; in three directions, cubical expansion. The former may be used in determining the latter, and will be the only measure considered.

The following is a list of linear expansions between 0° and 100° C.:

Platinum	0.000008842
Platinum (0° and 1000°)	0.00001015
Copper	0.000017182
Gold	0.00001466
Nickel	0.000016
Silver	0.000019097
Tin	0.00002173
Aluminum	0.00002313
Lead	0.000028575
Zinc	0.000029417
Bismuth	0.000013
Cadmium	0.000012
Iron	0.000012
Mercury	0.000181
Antimony	0.000017

There is generally a change in volume of a metal when it passes from the solid to the liquid state and the volume is altered during the fall of temperature between the point at

which the metal solidifies and until the temperature of the atmosphere is reached. Antimony, bismuth and copper are said to expand upon solidifying, and they also impart this property to their alloys. These metals are added to or admixed with other metals for the purpose of overcoming the contraction which occurs during the cooling process; by so doing a more perfect reproduction of a model in metal may be obtained. In considering the property of most metals of contracting upon cooling, great care must be exercised in pouring a molten metal into a mold: if the metal be poured at a temperature far above that of its fusing point, there will be a maximum amount of contraction produced when the metal is allowed to cool. To overcome this objectionable feature it is best to pour the molten metal at that temperature just above the melting point at which the metal just begins to lose its fluidity about the edges of the melting pot; or a better method is to use a pine stick and ascertain the point at which no vibrations are felt when the stick is immersed into the molten metal. This latter process is very serviceable in the case of casting zinc or lead in the construction of dies or counter-dies.

By comparing the coefficient of expansion of the metals with that of glass or porcelain bodies it will be found that platinum (with a coefficient of 0.000008842) and glass (0.000008513) are more nearly equal than in the case of any other metal with glass. The importance of this statement lies in the fact that it is often necessary to seal metals in glass or porcelain and it is impossible to obtain a perfect union of the metal and glass through the range of temperature that they have to pass if the metal contracts at a different rate than the glass or porcelain. The high cost of platinum during recent years has stimulated a great amount of research in this line of investigation to find some suitable substitute for platinum. It is frequently seen that alloys are made use of as a substitute for platinum in this capacity, in which the alloy has changed its form during the cooling process at such a rate that an imperfect joint between the alloy and the porcelain body results.

Porcelain teeth have been constructed in which the proper regard for this physical property of metals has been disregarded; the result, as might have been expected, was that the teeth lacked the proper resistance to the crushing force during mastication, and the pins of the teeth also were acted upon by the secretions of the mouth.

Another very interesting feature in regard to the application of this physical property of metals is the consideration of gold during the construction of cast inlays. Special precautions are taken in this operation, so as to prevent the shrinkage of the gold from changing the form of the inlay to such an extent as to render the inlay useless. In the construction of bridges it is necessary to prevent the shrinkage of the solder from changing the relative positions of the individual crowns which go to make up the piece. In extensive bridges the piece is soldered in sections and these in turn are then soldered together and in this way there is a minimum of force produced during the solidification and cooling of the solder; this in a great way prevents the contraction of the metal from warping the bridge.

Conductivity of Electricity.—Metals are the best conductors of electricity and are considered as a type for conductors; non-metals in some instances do not conduct a current and are said to be non-conductors. The temperature and also the purity of the metal has a direct influence upon its conducting powers of electricity. The following is a comparative list of the conductive powers of the various metals for electricity:—

Silver	100.00	Palladium	14.36
Copper	92.08	Platinum	13.44
Copper (hard)	90.05	Nickel	11.91
Gold	66.84	Tin	11.25
Aluminum	58.01	Thallium	8.15
Magnesium	33.70	Antimony	4.14
Zinc	25.52	Mercury	1.55
Lead	18.76	Bismuth	1.12
Cadmium	14.64		

The conducting power of the metals is best measured by a comparison of the resistance which the metals offer to the flow of a current. By considering this phase of the subject

absolute figures are obtained, while in the above list only a comparison is made. In considering the conductivity we assume that the flow of electricity through a conductor is analogous to the flow of heat; the flow of electricity being caused by a potential difference, as in the case of heat, it is due to a difference of temperature. The unit of resistance is taken as the resistance offered to an unvarying current by a column of mercury at the temperature of melting ice, 14.4521 grams in mass, of a constant cross-sectional area, and of a length of 106.3 centimeters. The cross-sectional area is 1 square millimeter.

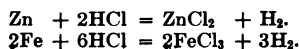
The resistance of a wire of uniform section = $p \frac{l}{s}$, l = length, s = cross-section, p = the specific resistivity of the metal.

The resistance of a metal increases as the temperature increases, the specific resistance may then be obtained for the various temperatures by the following equation $R_t = R_0 (15 + xt)$ where x = the temperature coefficient.

The following is a table of specific resistance of the metals expressed in microhms at 15° C. (Dewar and Fleming), also a table of temperature coefficients:

	P in microhms, 15° C.	Temperature coefficient.
Platinum	10.917	0.00367
Gold	2.197	0.00377
Silver	1.468	0.00400
Copper	1.561	0.00428
Aluminum	2.667	0.00435
Iron	9.056	0.00625
Nickel	12.323	0.00622
Tin	13.048	0.00440
Zinc	5.751	0.00406
Lead	20.380	0.00411

Replacing the Hydrogen of an Acid.—Most metals are soluble in the ordinary acids; the hydrogen being replaced and a salt of the metal formed. Hydrochloric acid reacts with a metal with the formation of a metallic chloride and the liberation of hydrogen,



Sulphuric acid is peculiar in its action upon certain metals and there may be two classes of reactions produced.

(a) In which hydrogen and a sulphate of the metal is formed, $\text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2$.

(b) In which sulphur dioxide, water and a sulphate of the metal is formed, $\text{Cu} + 2\text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$.

Nitric acid is far more complex in its reaction upon metals and the products formed are dependent upon the strength of the nitric acid and the property of the metal attacked. Hydrogen is rarely given off in the molecular condition, as the oxidizing power of nitric acid is so great that the moment hydrogen is liberated from combination it is oxidized to water (H_2O). As nitric acid is used extensively for dissolving metals, and also as it is the best solvent for them, the following will serve to illustrate a few of the important reactions of this acid upon metals:

(a) $3\text{Cu} + 8\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}$.

(b) $4\text{Zn} + 10\text{HNO}_3 \text{ (dil)} = 4\text{Zn}(\text{NO}_3)_2 + 5\text{H}_2\text{O} + \text{N}_2\text{O}$.

(c) $4\text{Zn} + 9\text{HNO}_3 \text{ (conc)} = 4\text{Zn}(\text{NO}_3)_2 + 3\text{H}_2\text{O} + \text{NH}_3$.

Antimony and tin are peculiar in their reaction with nitric acid; instead of the nitrates these metals form oxides and for this reason nitric acid is never used to dissolve these two metals when a solution containing antimony or tin is desired.

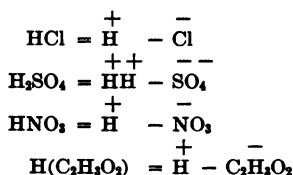
Platinum, gold, ruthenium, osmium, rhodium and iridium do not replace the hydrogen of an acid. With the exception of rhodium and iridium they are attacked by aqua regia (3 parts hydrochloric acid and 1 part nitric), but this is not by the replacement of hydrogen. Selenic acid (H_2SeO_4) is said to dissolve gold and the noble metals; however, this reaction is not made use of in the study of the metals.

Basic Oxides.—The prevailing idea is that metals form basic oxides only, but this, however, is not the case; all basic oxides are metallic oxides, but all metallic oxides are not basic. Chromium, manganese, iron and quite a few other metals form acid oxides. Those metals which form both varieties of oxides are said to possess acid and basic properties.

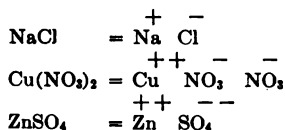
Ionization.—When the salts of the metals are dissolved in water they are broken up to a certain extent into extremely

fine particles called ions, which are of two varieties, (a) consisting of the metallic portion of the salt molecule, (b) consisting of the acid radicle. The metallic ion possesses the power of conducting a positive electrical charge (and in fact do possess a positive charge) when a current is passed through such a solution and is consequently known as a positive ion; on the other hand, the acid radicle ion is called the negative ion because it conveys the negative charge under like conditions.

The metallic salts are called electrolytes because of their property of conducting an electric current and may be distinguished from other substances by this fact. In very dilute solutions it is possible to have all of the salt ionized, while in more concentrated solutions there is a point of solubility for the salt in the molecular and also for the ionic condition. Considering how a substance is ionized, the following reactions will represent this phenomenon in its simplest form:

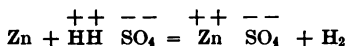


The degree of ionization is dependent upon the substance under consideration, the halogen acids are more completely ionized than the other acids and for this reason are considered the strongest of acids.



The above reactions represent how the metallic salts are broken up into ions when in solution.

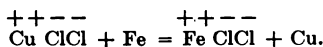
When a metal is acted upon by an acid the following illustrates the ionic condition of the substances:



The positive zinc ion replaces the positive hydrogen ion forming zinc sulphate, and the ions of which combine, the hydrogen ions at the same time discharge their positive charge and combine to form molecular hydrogen which leaves the solution as a gas, if the zinc sulphate formed is in such quantity as to exceed the degree of ionization of this salt it will crystallize from solution.

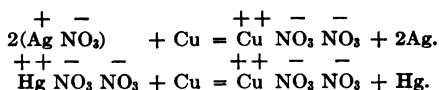
A solution of sodium chloride may be prepared and then hydrochloric acid gas passed through the solution; the sodium chloride will change from the ionic condition to the molecular state and will then fall out of solution. The phenomenon may be explained by the fact that hydrochloric acid is more readily broken up into its ions than sodium chloride; this causes the sodium ion to combine with the chlorine ion.

Another condition which may exist is that of a salt of a metal, say copper chloride, in solution to which metallic iron is added; the iron in this case goes into solution as Fe ions and the copper is deposited as metallic copper. The following ionic reaction represents the change:



The two positive charges of the copper ion is given up, the copper ceases to be an ion and assumes the molecular condition at the same time the iron takes up these positive charges as the iron (Fe ++ ion).

This reaction is used in obtaining metals from solution, and the following will illustrate a few other reactions of this type:



Ionic Chemical Changes.

1. Disunion and combination of ions. When a metallic salt is dissolved in water there is a disunion of the ions of which it is composed and upon evaporating the solution combination again occurs with the formation of molecules of the salt.

2. One ion may displace another. It has already been stated that the metallic ions may replace the hydrogen of an acid; one acid radicle may also replace another, as is shown by chlorine replacing bromine and iodine from their compounds. Metals react in the same manner toward each other, and the metallic elements may be arranged according to this property in a series designated as the electromotive series. The following is a list of metals arranged in this manner:

+

1. Alkali metals.
2. Alkali earth metals.
3. Magnesium.
4. Aluminum.
5. Manganese.
6. Zinc.
7. Chromium.
8. Cadmium.
9. Iron.
10. Cobalt.
11. Nickel.
12. Tin.
13. Lead.
14. Hydrogen.
15. Arsenic.
16. Copper.
17. Antimony.
18. Bismuth.
19. Mercury.
20. Silver.
21. Palladium.
22. Platinum.
23. Gold.

-

Some very interesting information may be gained by a close study of this list of metals as they are arranged, the metals occupying positions near the positive end will replace a metal located lower in the list from combination. The metals above hydrogen are classed as positive while those below are classed as the negative ones, as regards their behavior toward the metals above hydrogen.

Metals Nos. 1, 2, 3 are unstable in air; Nos. 1, 2, 3, 4 are not reduced from their compounds (oxides) by heating in a stream of hydrogen; Nos. 1 to 13 never occur in the free state in nature, they replace the hydrogen ion of an acid, and Nos. 4 to 13 are the base metals which form stable oxides. Nos. 15 to 23 do not replace the hydrogen of acids, found in the free state in nature, while Nos. 19 to 23 are the noble metals and form unstable oxides.

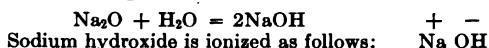
When two of the metals are immersed in a solution of an electrolyte in which one of the metals is more readily acted upon than the other by the solution, a so-called voltaic couple is formed, the greater the distance between the metals in the electromotive series the greater will be the potential difference existing between the metals. This principle is made use of in the construction of a wet cell. If two metals are placed in the mouth in which there exists a great potential difference, an electric current will be produced; this current is found to have a direct action upon tooth structure, particularly if the metals are fillings in the teeth.

The saliva contains inorganic salts in solution which act as electrolytes.

Much agitation has been created recently in regard to the employment of such metallic combinations in dental amalgam alloys and the question as to the deleterious effects of these alloys is still subject to dispute; from a practical point of view, however, such alloys should not be used.

The explanation why some of the metallic oxides are basic oxides is rather simple, when it is considered that, a "base" is a substance which liberates negative hydroxyl ions on solution.

When a metallic oxide is treated with water the following phenomenon takes place:



This same reaction may be written for any of the basic oxides.

Electrolysis.—When an electric current is passed through a solution of an electrolyte the current is carried through the solution by the ions of the salt. The metallic elements convey the positive charge from the positive electrode to the negative electrode and may then be discharged; at the same time the negative ions of the salt convey the negative electricity to the negative pole and are discharged. The metallic ions are thus found at the negative pole (cathode) and are called cations, while the negative ions found at the positive pole (anode) and are called anions.

The electrical power consumed in this operation is exceedingly small and advantage is taken of this in obtaining metals from their compounds. The metals so obtained are in an exceedingly high state of purity.

Faraday established the fundamental laws on electrolysis and the subject of electrolysis would hardly be complete without mentioning these in explanation of this phenomenon.

Faraday's Law.—When the same quantity of electricity is passed through different electrolytes the ratio between the quantities of the liberated products of electrolysis is the same as that between their chemical equivalent.

If solutions of silver nitrate, gold chloride and copper sulphate be introduced into the same electric circuit it will be found that the metals will be deposited at the cathode and in such quantities as their equivalent weights, that is, their atomic weight divided by their valency in the compound; thus: 108 grams of silver, 31.7 grams of copper and 65.66 grams of gold.

The quantity of electricity required to liberate 1 gram of hydrogen taken as the unit, then the number of units required to liberate the atomic weight of the various other elements may be obtained by dividing the equivalent weights of the elements into their atomic weights.

The quantity of electricity which is carried by one gram of hydrogen as the unit was determined as 96,540 coulombs. Then when an element is represented with two plus marks it signifies that such element will carry 2 times 96,540 coulombs of electricity.

If it be required to deposit 108 grams of silver in one hour the amperage of such a circuit may be determined by dividing the coulombs (96,540) by the time in seconds (60×60) giving 27.9 amperes of current strength necessary for such a deposit in the time mentioned.

From these facts the following facts were developed:

(1) The mass of the ions liberated at either pole is proportional to the quantity of electricity which passes any section of the circuit.

(2) The mass of the ions liberated at either pole is proportional to the chemical equivalent of the ion, *i. e.*, atomic weight divided by the valency of the element in the compound.

It would take us too far into physics to develop these laws, although electrolysis is of importance in the recovery of metals, electroplating and other metallurgical operations. Those especially interested in this phase of the subject may consult text on physic and electrochemistry.

Potential Difference.—The metals have a certain solution tension which tends to force them into solution. This force or tension gradually diminishes from the positive to the negative end of the electromotive series. If the ions of the metal are present in the solution already, they tend to give up their electrical charge and deposit themselves upon the metal. The tendency of the metal ions to be deposited and give up their charge is directly due to their osmotic pressure in the solution. The osmotic pressure of a solution containing the molecular weight in grams of a salt is 22.4 atmospheres.

Determinations have been made with normal solutions, *i. e.*, those containing the equivalent of one hydrogen in grams of the salt to the liter of water. A bar of the metal was immersed in the solution of its salt and in this condition it is found that the metallic ions in the solution possess a positive charge, while the metallic bar has a negative charge.

POTENTIAL DIFFERENCES IN VOLTS FOR NORMAL SOLUTIONS OF CATIONS
(ALEX. SMITH).

Magnesium	+1.21	Lead	-0.13
Aluminum	+1.00	Hydrogen	-0.28
Manganese	+0.80	Copper (Cu π) . .	-0.61
Zinc	+0.49	Arsenic	-0.62
Cadmium	+0.14	Bismuth	-0.67
Iron (Fe π)	+0.06	Mercury	-1.03
Thallium	+0.04	Silver	-1.05
Cobalt	-0.04	Palladium	-1.07
Nickel	-0.04	Platinum	-1.14
Tin	-0.08	Gold	-1.35

If a strip of silver be placed in a solution of silver nitrate (normal solution) the silver ions from the nitrate possess a positive charge and the strip of silver a negative charge; the difference between these two charges determines the electrical condition of the solution, in this case the solution will be found to have a negative charge of—1.05 volts.

Considering two of these metals immersed in a solution, such for example as sulphuric acid, it will be found that the following couples produce very nearly the following values:

Silver-zinc,	- 1.05 + 0.49 = 1.54 volts
Copper-zinc,	- 0.61 + 0.49 = 1.10 volts
Tin-zinc,	- 0.08 + 0.49 = 0.57 volts
Mercury-zinc,	- 1.03 + 0.49 = 1.52 volts

In testing dental amalgams Crandall reports the following figures for amalgams containing zinc and compares these figures with those in which a non-zinc dental amalgam alloy was used, in the amalgam,

Zinc alloy amalgams range from 20 to above 25 millivolts.

Non-zinc amalgams ranged from 1.75 to 2 millivolts.

These figures were obtained from amalgams free from corrosion of the saliva, after the fluids of the mouth had acted upon the amalgam the zinc amalgams showed a smaller deflection of the galvanometer than before.

The subject of electrolysis and ionization is attracting much interest at the present time in dentistry and it is well to bear in mind the difference between the two terms. Whenever a

metallic salt goes into solution, ionization is produced, but for electrolysis to be produced an electric current must be passed through the solution.

Odor and Taste.—Odor and taste are possessed by a few of the metals. Iron, copper and zinc when heated evolve peculiar odors. Iron when treated with acids sometimes evolves an odor, but this is due to hydrocarbons as impurities in the iron. Arsenic gives off an alliaceous odor (garlic-like), and the recognition of which is one means of detecting arsenic. Odor and taste may in some instances be explained: as in the case of alloys, or the presence of two metals in the mouth, forming a voltaic couple, compounds of the metals would be formed, which would affect the taste buds on the tongue. A similar phenomenon, in the case of mixing amalgams in the hand, producing metallic compounds, gives rise to an odor.

Specific Heat.—When metals are heated they take up heat. The quantity necessary to raise them through one degree of temperature differs in each individual metal. The quantity of heat necessary to raise one gram of metal through 1° C. of heat is called its specific heat. Water has the greatest capacity for heat, and the quantity of heat necessary to raise it through 1° C. is taken as the standard. The following is a list of specific heats of the metals between 0° and 100° C.:

Aluminum . . .	0.2143	Lead	0.0314
Antimony . . .	0.0513	Magnesium . . .	0.2475
Arsenic	0.0822	Mercury	0.0332
Bismuth	0.0308	Nickel	0.1092
Cadmium	0.0567	Platinum	0.0324
Cobalt	0.1067	Potassium	0.1655
Copper	0.0968	Silver	0.0570
Gold	0.0324	Tin	0.0555
Iron	0.1138	Zinc	0.0950

The specific heat of water is taken as 1000 and it requires one calorie of heat to raise the temperature of one gram of water through 1° C., then from the above table it will require the corresponding number of calories of heat to raise a gram of the metal through 1° of temperature, or it might be explained by using some metal, say gold for example, with a specific heat of 0.0324, then it will require 0.0324 calorie of heat to

raise one gram of gold through 1° centigrade. The specific heat of the metals depends upon their physical condition, hard copper differs from the softer variety in its specific heat. The temperature has also a direct influence upon this property of the metals, the specific heat is greater between 200° and 300° than between 0° and 100°. Any agency which tends to increase the density of a substance diminishes its specific heat.

The specific heats of the metals are of value for two purposes; they indicate the quantity of heat which is necessary to raise a metal through a given range of temperature, and secondly, they are of importance in proving the atomic weight assigned to a metal is correct. The specific heat divided into 6.4 gives approximately the atomic weight of the metal, for example,

$$\text{Gold sp. heat} = 0.0324, \text{ then } \frac{6.4}{0.0324} = \text{at. wt. } 197.5$$

and the atomic weight of gold by experimentation is 197.2.

The factor 6.4 is obtained by multiplying the atomic weight of the elements by the specific heat; this figure is the average for determinations made upon the various elements and is called the atomic heat.

Specific Gravity.—This term denotes the comparison of the weight of equal volumes of two substances under the same conditions of temperature, one of them being taken as a standard. For solids and liquids, distilled water is the standard. It is the tendency to drop this term at the present time as the density of a substance in metric weights also expresses its specific gravity. If the volume of a substance is known then, by simply weighing it in the metric system and calculating the weight of a cubic centimeter we also have the specific gravity.

$$\text{Density} = \frac{\text{mass}}{\text{volume}}.$$

The specific gravity of a metal is, as a rule, not subject to change, but the physical condition of the metal tends to alter its specific gravity. Precipitated, cast, and rolled gold, all have different specific gravities.

The lightest metals belong to the alkali group; they are lighter than water, and at the other extremes osmium is

generally considered one of the heaviest of elements. The following is a list of specific gravities:

Lithium	0.59	Cobalt	8.5
Potassium	0.875	Cadmium	8.6
Sodium	0.97	Molybdenum	8.6
Rubidium	1.52	Nickel	8.8
Calcium	1.58	Copper	8.8 to 8.9
Magnesium	1.74	Bismuth	9.82
Aluminum	2.56	Tantalum	10.8
Zirconium	4.15	Thorium	11.1
Selenium	4.3	Palladium	11.5
Vanadium	5.5	Rhodium	12.1
Arsenic	5.67	Ruthenium	12.26
Tellurium	6.25	Uranium	18.7
Antimony	6.72	Tungsten	19.2
Chromium	6.8	Platinum	21.5
Zinc	6.86 to 7.2	Iridium	22.42
Tin	7.29	Osmium	22.48
Manganese	7.4	Lead	11.38
Iron	7.7 to 8.1	Mercury	13.59
Silver	10.42 to 10.52	Gold	19.3 to 19.5
Thallium	11.9		

Color.—The color of the metals depends upon the physical condition in which they exist. In the compact form, as we usually see them, they present a range of color from white of silver to deep blue of lead. The color of compact metals can be classed as follows:

White	Silver	Pale yellow	Barium
	Mercury		Strontium
	Zinc		
	Tin		
	Sodium		
Blue	Aluminum	Deep yellow	Calcium
	Lead	Rich yellow	Gold
	Platinum		
	Iron		
	Antimony	Pink	Copper

In powder, or amorphous form, their color becomes entirely changed; gold becoming brownish yellow; silver, grayish white; copper, yellowish red; and platinum, black.

Some of the metals can be obtained in an extremely fine divided state, as a colloidal solution, and when viewed with the ultramicroscope the solution proves to be a suspension of shining metallic particles. Under this condition platinum

makes a brown solution; gold, bluish red; silver, when dry; bluish or green; silver, when dissolved in water, deep red, mercury, black.

Colloids have been defined as substances in solution which could be separated from crystalloids by dialysis. Mathews has classed the colloidal metals as suspensoids, because they do not possess the property enabling them to gel, and furthermore, has classed colloids into two groups, viz., emulsoids and suspensoids. The colloids being defined as substances which in solution gives particles ranging from 1 to 100 uu (uu = one thousandth of a micron) in linear dimensions.

The following is the size of some of the metals in this condition:

Gold	6 to 130 uu.
Silver	50 to 77 uu.
Platinum	44 uu.

The particles of a colloidal metal in solution are electro-negative.

In the vapor form the metals in some instances impart colors to the flame, as in the so-called flame or spectroscopic tests. In most cases these colors are produced by the vapor of a volatile compound of the metal rather than the metal themselves.

Potassium gives violet flame.
Sodium gives yellow flame.
Lithium gives red flame.
Barium gives yellowish-green flame.
Calcium gives reddish-yellow flame.
Copper gives green or blue flame.
Tellurium gives pure green flame.
Thallium gives pure green flame.
Zinc gives whitish flame.
Arsenic gives light blue flame.
Strontium gives scarlet flame.

By means of the spectroscope these metals may be positively identified by the characteristic color bands produced. These bands may be recognized even in the case of mixtures of the various metals. This is the only positive method of identifying such metals as those belonging to the alkali group, as they do not, as a rule, give characteristic precipitates with the various reagents usually used in analytical chemistry.

Malleability, Ductility, and Tenacity.—The qualities of malleability, ductility, and tenacity differ widely in the metals. The term malleability, when applied to such a metal as gold, signifies that by hammering or rolling its surface may be extended in all directions, and that it is capable of being thus reduced to very thin leaves or sheets without fracture of its continuity at the edges during the process of attenuation; when applied to other metals the term should be understood as expressing this quality relatively. Gold is the most malleable of the metals and is capable of being made into leaves of $\frac{1}{367650}$ of an inch in thickness, each grain of which will cover a surface of seventy-five square inches.

The property of malleability and that of brittleness are directly dependent upon the hardness and crystalline condition of the metals. Bismuth, antimony, and arsenic, which are absolutely crystalline metals, are so brittle that they fly to pieces when struck with the hammer, and they can be finely powdered in a mortar. Formerly malleability and ductility were considered as essential properties of a metal, but this is no longer the case, as bismuth and antimony disprove the rule.

Malleability also presupposes a certain degree of softness, toughness, and a total obliteration of crystalline structure.

The degree of malleability is greatly influenced and dependent upon the temperature. Most of the metals become more malleable and softer when heated. Iron, for instance, is most malleable at red heat. Zinc is crystalline and not very malleable at ordinary temperatures, but at 100° to 150° C. it is quite malleable, and at 200° C. it again becomes brittle. Frozen mercury is also malleable.

There are no methods of determining the absolute values of malleability and ductility; however, the lists published give an idea of what may be expected of a metal when submitted to the processes of rolling or being passed through the draw plate. As to the absolute values of a table of this kind, it is found that our methods of measuring these properties fail before the limit of malleability or ductility has been reached.

Malleability, ductility, and tenacity depend upon the

property of cohesion and that phase of cohesion known as solid flow. The mechanical procedures used in rolling, drawing, or the application of forces tending to cause the rupture of a metal cause the rearrangement of the molecules. In the case of some metals the crystalline structure permits of the rearrangement without overcoming the force of cohesion of the molecules. The effect of these distorting forces produces an abnormal condition between the molecules and as a result the metals become more brittle. Heating the metals after such treatment tends to restore the original softness to the metal.

In the following list by Regnault¹ the metals are arranged in the order of their malleability:

- | | |
|--------------|-----------------------|
| 1. Gold. | 8. Zinc. |
| 2. Silver. | 9. Iron. |
| 3. Tin. | 10. Nickel. |
| 4. Copper. | 11. Palladium. |
| 5. Cadmium. | 12. Potassium. |
| 6. Platinum. | 13. Sodium. |
| 7. Lead. | 14. Mercury (frozen). |

Ductility signifies that property which renders a metal capable of being drawn into rods or wires, usually accomplished by passing an elongated piece of metal through a series of gradually diminishing holes in a steel draw-plate; the granular particles of the metal are thus extended into fibers. One grain of gold has been drawn into a wire 550 feet long. To accomplish this result a compound wire is made of gold covered with silver, the tenacity of the latter being taken advantage of to enable the gold to be carried through the successive holes of the draw-plate until the greatest possible attenuation is reached; after which it is immersed in nitric acid, which dissolves the silver, leaving a gold wire $\frac{1}{5000}$ of an inch in diameter. By the same method Wollaston drew out a platinum wire $\frac{1}{30000}$ of an inch in thickness.

All malleable metals are ductile, but malleability and ductility are not necessarily proportional to each other.

Ductility depends upon toughness and tenacity, otherwise the force needed to draw a metal through the draw-plate

¹ Phillips's Metallurgy, p. 412.

would rupture it. Heat affects ductility, rendering some metals quite workable and decreasing this property in others. Hammering and drawing change the molecular structure of metals and greatly influence their physical properties, rendering them denser, harder, more elastic, and brittle. In rolling plate and drawing wire it is necessary to keep the metals at their proper degree of softness, therefore we must anneal them frequently.

In the following table the metals are arranged according to the ductility:¹

- | | |
|--------------|----------------|
| 1. Gold. | 6. Zinc. |
| 2. Silver. | 7. Tin. |
| 3. Platinum. | 8. Lead. |
| 4. Iron. | 9. Nickel. |
| 5. Copper. | 10. Palladium. |
| | 11. Cadmium. |

Tenacity is the power possessed by metals to sustain weight, and to resist rupture, when a bar or rod is exposed to tension. Various kinds of tenacity are recognized according to the nature of the externally acting force: *ordinary* tenacity, resistance to traction; *relative* tenacity, resistance to fracture; *reactive* tenacity, resistance to crushing; *shearing* tenacity, resistance to lateral displacement; *torsional* tenacity, resistance to twisting.

As the fitness of metals for certain purposes in the industrial arts depends largely upon this property, it is of the utmost importance to know the comparative tenacity, not only of the different metals but of the different alloys.

In determining the comparative tensile strength of metals it is customary to take bars of the metals of equal length and equal diameter and to determine the number of pounds weight required to cause their rupture. This is usually accomplished by means of a testing machine constructed on the compound-lever principle.

In subjecting metal bars or wires to a certain amount of tension, an elongation of the wires takes place. If this degree of tension is not overstepped they will return to their original length; but if the tension is carried beyond this

¹ Platinum should be classed above gold in accord with Wollaston's determinations.

point a permanent elongation takes place, in which case the *elastic limit* of the metal has been passed. In the technical use of metals where they have to withstand great strains, as in elevator ropes or in chains, it is of the utmost importance that the strain should never go beyond the elastic limit, because certain molecular changes take place in the metals, resulting from the permanent elongation. These changes greatly weaken the tensile strength of the metals and might result in accidents.

Tensile strength is diminished by continuous strain. If a wire is subjected to a low strain continuously it will finally break, when a much greater strain would not have caused its rupture at first. Tenacity is also influenced by the shape of the body; for instance, a hollow cylinder is much stronger than a solid one, provided the quantity of metal is the same in both.

Elevation of temperature, even within rather circumscribed limits, affects the tenacity of metals to a marked degree, generally *diminishing it*.

Alloying increases tensile strength, as is instanced in the case of brass, which has a greater tenacity than either of its components, copper and zinc. Heat destroys this property greatly.

The following table¹ gives the results of experiments on the tensile strength of a few of the metals at temperatures between 15° and 20° C.:

FOR WIRE OF 1 SQ. MM. SECTION, WEIGHT (IN KILOS) CAUSING		
	Permanent elongation of 1/2000.	Rupture.
Gold, drawn	13.5	27
Annealed	3.0	10
Silver, drawn	11.3	29
Annealed	2.6	16
Platinum, drawn	26.0	37
Annealed	14.0	23
Copper, drawn	12.0	40
Annealed	under 3.0	30
Iron, drawn	32.0	61
Annealed	under 5.0	47
Palladium, drawn	18.0	37
Annealed	under 5.0	27

¹ Annales de chimie et de physique (III), vol. viii, Wertheim.

The following table shows the relative order of the metals in their capacity for sustaining weight:

- | | |
|--------------|----------|
| 1. Iron. | 5. Gold. |
| 2. Copper. | 6. Zinc. |
| 3. Platinum. | 7. Tin. |
| 4. Silver. | 8. Lead. |

It has been observed that students and others very often fail at first to appreciate the difference between these properties, and they not infrequently fall into the mistaken idea that the three qualities of malleability, ductility and tenacity are possessed to an equal extent by each metal. If, however, we take gold for example—the most perfectly malleable and ductile of the metals—we shall find that in tenacity it ranks considerably below some of the others, and the greatest care is necessary in drawing a piece of gold into even a moderately fine wire, and beyond a certain limit, past which platinum or copper may be carried with safety; gold would not possess sufficient tenacity to overcome the resistance to which it would be exposed in passing through the smaller holes of the draw-plate, and fracture would result.

Iron, on the other hand, which exceeds all of the other metals in tenacity, is in malleability inferior to gold, silver, copper, platinum, lead, zinc, tin, and cadmium.

It is stated that brass drawn into wire will often, after a time, become crystalline in texture and brittle by slow change of molecular arrangement.¹

Hardness.—Hardness is that property of the metal which resists a change in the relative position of the molecules of the metal without separating them from each other.

Hardness may therefore be tested and recorded as the resistance to indentation.

There are a number of methods for testing hardness, but the one of Ballentine is probably the best, and depends upon the following fact: that a known and constant weight, which is allowed to fall through a known and constant distance, will exert a known and constant force upon an anvil, which,

¹ Makins's Metallurgy, p. 10.

if the force is transmitted to a pin which is capable of indenting the material tested, the relative hardness of the materials can be determined by the depth of the indentation.

Density Hardness.—By this is understood the hardness produced in pure metals or alloys by compression, rolling or hammering. The hardness of a metal is not necessarily proportional to its density. The densest metals may be either hard or soft, as shown in the case of iridium (specific gravity 22.4), which is a fairly hard metal, while gold (specific gravity 19.3), platinum (specific gravity 21.5), and lead (specific gravity 11.38) are certainly very soft. Experiments show that density hardness, produced by compression, depends upon both ductility and strength of a metal.

	Original hardness.	Hardness after compression.
Copper, cast	6	20
Brass, cast	12	26
Brass, hard	30	35
Iron, wrought	18	30
Iron, gray	40	41
Steel, annealed	30	45
Zinc	8	20
Type metal	20	21½
Babbitt metal	5	6½
Babbitt metal, extra hard	9	8
Lead	2	3

These figures show the copper gaining 300 per cent. in hardness by compression, while the cast Babbitt metal loses some of its initial hardness.

The study of compression hardness is of prime importance in selecting metals for bearings which will be subjected to great shocks or compression.

Crystallization.—Crystallization is the process by which the molecules of a substance arrange themselves in geometrical forms when passing from a liquid or gaseous to the solid state. Many substances are capable of crystallization. The crystals formed are very definite in their characters, and can be used like any other physical properties in distinguishing one substance from another. Some substances crystallize in two distinct forms, and they are then said to be dimorphous. The outward shape of a crystal is its most striking feature, but this form is only an external expression

of a regular internal structure. Many crystals occur in very complicated forms, so that at first sight it would seem impossible to recognize them, but by careful study they can be simplified and referred to one of six systems. To be able to classify and compare the forms of crystals we must have some simple mode of expressing the relative positions and inclinations of their planes. This is accomplished by referring them to systems of axes, according to the method of analytical geometry. The position of any crystal plane is thus fixed by and expressed in the relative lengths of its intercepts in the axes to which it is referred. The axes to which the planes of a crystal are referred, called the crystallographic axes, may be of equal or unequal length, and may intersect at either oblique or right angles. The six *crystal systems* are:

1. *The Isomeiric or Regular System.*—All the forms referable to this system have three axes (imaginary lines passing through the solid angles of the octahedron) of equal length, intersecting at right angles.

Examples: Regular octahedron, hexahedron (cube) rhombic dodecahedron, etc.

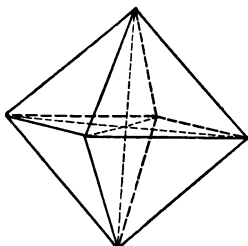


FIG. 2.—Octahedron.

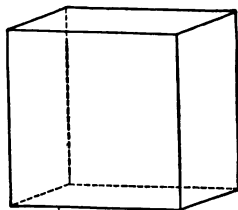


FIG. 3.—Cube.

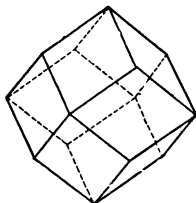


FIG. 4.—Rhombic dodecahedron.

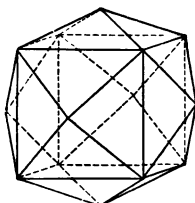


FIG. 5.—Tetrahexahedron.

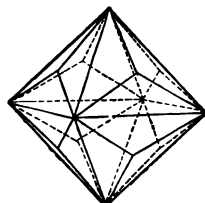


FIG. 6.—Trisocahedron.

2. *The Tetragonal or Quadratic System.*—All forms referable to three axes at right angles to each other, two of equal length, the third or principal one having a variable length.

Examples: Tetragonal pyramids, tetragonal prisms.

FIG. 7

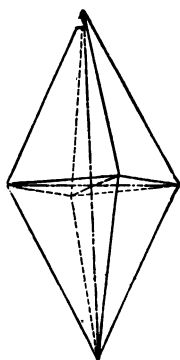
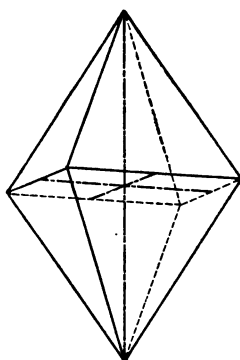


FIG. 8



FIGS. 7 and 8.—Tetragonal pyramids.

FIG. 9

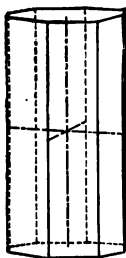


FIG. 10

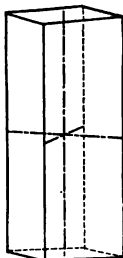
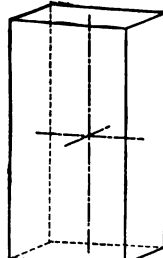


FIG. 11



FIGS. 9, 10 and 11.—Tetragonal prisms.

3. *The Hexagonal System.*—All forms referred to four axes—three lateral axes of equal length, inclined at angles of 60 degrees to each other, one principal axis at right angles to the other three and having either the same or a different length.

Examples: Hexagonal pyramid and hexagonal prism.

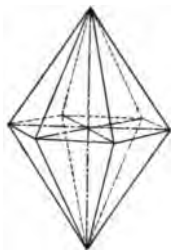


FIG. 12.—Hexagonal pyramid.

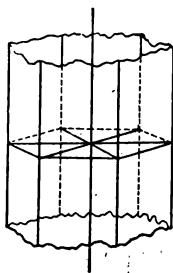


FIG. 13.—Hexagonal prism.

4. *The Orthorhombic System.*—All forms referable to three axes of unequal length intersecting at right angles.

Examples: Orthorhombic prism and orthorhombic pyramid.

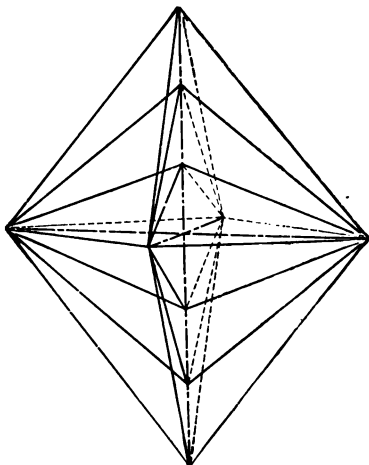


FIG. 14.—Orthorhombic pyramid.

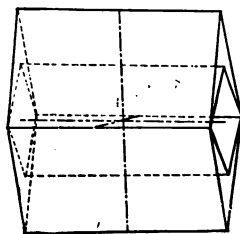


FIG. 15.—Orthorhombic prism.

5. *The Monoclinic or Oblique System.*—All crystals have axes of unequal length—two at right angles to each other

and the third at right angles to one and inclined to the other.

Examples: Monoclinic pyramids and prisms.

6. *The Triclinic or Asymmetric System.*—The crystals belonging to this system are referred to three axes of unequal length, all inclined to one another.

Examples: Triclinic prisms and pyramids.

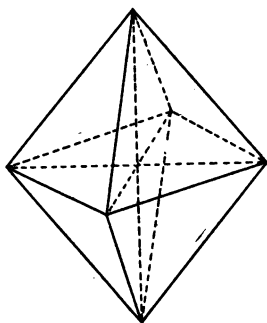


FIG. 16.—Monoclinic pyramid.

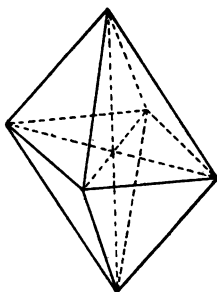


FIG. 17.—Triclinic pyramid.

It is stated that under favorable circumstances all the metals will assume a crystalline form. It is known that some of them, as gold, silver, etc., are found native as cubes or octahedra, or in slight modifications of these forms; and metals in a crystalline form may be obtained by electrolysis, as, for instance, silver or lead, while a condensation of the vapors of zinc or cadmium will produce crystals of these metals. Metals with low fusing points, such as bismuth or antimony, will crystallize on cooling after they have been melted. Nearly all the metals yield crystals when deposited from their solutions by electric currents of feeble intensity. The beautiful preparation known as Watt's Crystal Gold is formed in this way. Gold so prepared is generally in a high state of purity.

Highly crystalline metals exhibit peculiar appearances on their fractured surfaces. These are quite constant for the

individual metals, and can be taken as indicating the purity of the metals. The varieties of fractures are:

1. Crystalline: as zinc, antimony, and bismuth.
2. Granular: steel.
3. Fibrous: wrought iron.
4. Silky: copper.
5. Columnar: grain-tin.
6. Conchoidal: native arsenic.

Native metals crystallize in the following systems:

Palladium	Rhombohedral	Lead . . .	Isometric
Arsenic .	"	Copper . . .	"
Magnesium .	"	Mercury (solid)	"
Antimony .	"	Platinum . .	"
Zinc . . .	"	Iron	"
Bismuth . .	"	Tin	Quadratic
Gold . . .	Isometric	Potassium . .	"
Silver . . .	"		

Sonorousness.—Sonorousness may be defined as that property possessed by a substance of emitting a sound when struck. Most of the metals in a pure state do not possess this property, but upon alloying with other metals acquire it. Aluminum is an exception to the rule and is used instead of parchment in drum-heads. One of the first articles constructed of aluminum was a child's rattle for one of the nobility of Europe. To show the effects of alloying upon metals, iron does not possess this property until combined with the proper amount of carbon, when it will be found that it gives off a musical sound when struck. Tin and copper, neither being sonorous, when alloyed form bell metal.

Elasticity is that property possessed by a substance by virtue of which it returns to its normal position after a disturbing force has been applied. The measure of elasticity, so-called coefficient of elasticity, is determined by the following formula:

$$\text{Coefficient of } E = \frac{\text{stress}}{\text{strain}} .$$

A substance which requires the greatest force to produce the least distortion will evidently have the greatest coeffi-

ciency. The popular belief that rubber is the most elastic substance is an error, because the smallest amount of stress will produce a great strain, and on referring to the above formula it will be seen that the coefficient will be small.

Platinum is added to gold, although both metals have a low coefficient of elasticity; the resulting alloy possesses elasticity to such an extent that it is used for clasps for artificial dentures. Platinum and iridium alloy—the iridium being present in small quantities—forms an elastic alloy, which is sometimes used for the construction of metallic bases for artificial dentures.

Magnetism.—Although the ancients were aware of the fact that when magnetite or loadstone was brought near or in contact with iron, there was an attractive force which held them together so that a variable degree of tension was required to pull them apart; furthermore, that this property was transmitted from the loadstone to the iron; nevertheless, it was only after the invention of the mariner's compass that magnetic science made any progress.

A magnet has two poles, and if it is suspended so that it can swing freely, these poles will always arrange themselves in a definite relation to the geographical axis of the earth, one pointing north, the other south.

Whenever an electric current flows in a closed circuit the surrounding space becomes a field of magnetic force, and any piece of iron in it will become inductively magnetized. Such an arrangement of an electric circuit and iron is called an electromagnet.

When magnetism is induced, a certain proportion of magnetism usually remains after the inducing force is removed. This happens even with the softest iron, if the inducing force is very great. In different bodies the power of retaining magnetism varies as much as the inductive susceptibility. Thus, while the inductive susceptibility of steel is less than that of iron, it retains much more of the magnetism imparted to it, and the harder the steel is tempered the greater will be the coercive force or retaining power. Increase in temperature diminishes magnetism, and

red heat destroys it in all bodies but cobalt, the latter requiring a white heat to effect this result.

The two varieties of magnetism spoken of as paramagnetism and diamagnetism, respectively, mean attraction or repulsion to the magnet.

Paramagnetic metals are iron, nickel, cobalt, manganese, chromium, palladium, platinum, and osmium.

Diamagnetic metals are bismuth, antimony, zinc, tin, cadmium, sodium, mercury, lead, silver, copper, gold, etc.

The magnetism of metals is undoubtedly largely influenced by impurity. The commercial copper, for example, is paramagnetic owing to the presence of traces of iron; but when it is reduced by means of zinc from chloride or sulphate, it is diamagnetic.

Agents which May Volatilize a Metal.—Concentration of solar rays in the focus of a lens; the voltaic current; the oxyhydrogen blow-pipe flame; oxyacetylene blow-pipe flame.

M. Depretz employed the first three in conjunction, by which means he volatilized magnesium, and with a powerful Bunsen battery alone he reduced carbon by volatilization to the state of a black powder.¹

Opacity.—Opaque bodies do not transmit light. No bodies are absolutely opaque; however, metals, as a rule, absorb the rays of light which fall on them, and a few allow some of the rays to pass through. Gold in a highly attenuated condition transmits green light; silver and a few others also transmit light.

Occlusion.—Occlusion is that property possessed by a metal of absorbing gases.

The metals, though destitute of physical pores, possess the property of absorbing gases either on their surfaces or in their mass. This may be observed when a metal is heated and then allowed to cool in contact with the gas. Platinum occludes four times its volume of hydrogen and 4.15 volumes of carbon monoxide. Silver, reduced from the oxide, absorbs about seven times its volume of oxygen, and nearly one

¹ Percy's Metallurgy.

volume of hydrogen when heated to dull redness in these gases.

Palladium absorbs 980 times its volume of hydrogen at red heat, and at ordinary temperature 376 times its volume. The following list shows the volume of hydrogen absorbed by some of the metals:¹

Palladium, black	502.35	Nickel	17.57
Platinum, sponge	49.3	Copper ,	4.5
Gold	46.3	Aluminum	2.72
Iron	19.17	Lead	0.15

Molten silver occludes about twenty-two times its volume of oxygen, which is given up again (with the exception of 0.7 volume) on solidification. As the mass cools, the oxygen evolved often bursts through the outer crust of solidified metal with considerable violence, ejecting portions of the still liquid silver as irregular excrescences; this is known as the spitting of silver. Small quantities of admixed metals prevent the absorption of oxygen.

This fact must be borne in mind when silver is used in cast work. I have had several inquiries as to the cause of failure on the part of practitioners in using silver to cast root restorations.

Welding.—Welding is the process of joining two metallic surfaces by the aid of heat and pressure. Pure gold may be welded in the cold. Iron requires a white heat in order to be welded.

Fusion or Autogenous Welding.—Fusion or autogenous welding is accomplished by an intense heat concentration at the location of the weld. Its object is to bring the metal, at the point of treatment, to a liquid state, so that the two bodies of metal to be joined will flow or fuse together, as distinguished from the joint made by pressure or blows. Fusion welding, as usually practised, employs heat generated either by electricity or by the burning of a combustible gas with oxygen. For the combustible gas, hydrogen, coal gas or acetylene is generally used.

¹ Neuman and Stientz.

Electric Welding.—There are two distinct forms of electric welding, commonly known as the resistance and arc processes.

Goldschmidt's Process of Welding.—When a mixture of finely divided aluminum is mixed with certain oxides (iron oxide or chromium oxide) and the mass ignited by a fuse, the aluminum takes the oxygen from the other metallic oxides, liberating these metals in a fused condition. The temperature of about 3000° C. is reached in a very short period of time. This process is sometimes spoken of as "thermite welding."

Swaging.—Swaging is the process of adapting a lamina of a metal to conform to a desired shape, by the uses of a die and counter-die by pressure.

Forging.—Forging is a process of hammering a metal into various shapes. Both of these processes are dependent upon the physical power of the molecules of a metal known as "solid flow." The molecules of a metal by virtue of "solid flow" may change their relative positions without overcoming the force of cohesion.

Flotation.—Flotation is the process of adding oils to metal-bearing substances during the operation of concentrating ores. By this process it is found that certain minerals may be recovered from tailings and in this manner cause a more complete recovery of the metal from its ores. This branch of metallurgy has been but recently developed and some of the peculiarities of the process are that certain oils when agitated with minerals cause a frothing; the oil contains the mineral of some certain metal. For example, an ore containing zinc and lead; an oil may be used which will cause the flotation of the zinc and the lead will not be acted upon, and on the other hand, another oil would cause the flotation of the lead. The character of these phenomena is not thoroughly understood and it cannot be predicted which oil will cause a flotation with any certain metal. Experimentation alone will determine this point.

Atomic Volume.—The atomic volume of the metals is sometimes made use of in the process of alloying. Attempts are

made in this manner to bring about a more perfect equilibrium between the atoms of the metals entering the alloy.

The atomic volume of the metals is determined by dividing the atomic weight by the specific gravity. The figures do not express the comparative volumes of the atoms of the substance but the space occupied by the atoms plus the inter-atomic spaces.

The following is a list of atomic volumes (Price & Fahrenwald):

Aluminum	10.4	Mercury	14.0
Antimony	18.1	Molybdenum . . .	10.6
Bismuth	21.2	Tungsten	9.8
Cadmium	13.0	Nickel	6.5
Chromium	7.5	Osmium	8.4
Copper	7.1	Palladium	8.9
Gold	10.2	Platinum	9.06
Iridium	8.6	Silver	10.2
Iron	7.1	Tin	16.3
Lead	18.2	Zinc	9.2

In constructing alloys of the metals, as a rule the proportions are calculated according to mass or weight; however, if it be desired to consider the atomic structure, so that the conditions present in the alloy will more nearly approximate the condition present in a chemical compound, a nearer approach to this condition can be obtained by a consideration of the atomic volumes of the metals.

CHAPTER IV.

ALLOYS.

AN alloy is a substance formed by the bringing together of two or more metals in the state of fusion.

The phenomenon which takes place when metals are brought together in the state of fusion is a very complex one. According to the older views on this subject the resulting substance may be (Matthiessen):

1. A solution of one metal in another.
2. A chemical compound.
3. Mechanical mixture.
4. A solidified solution or mechanical mixture of two or all of the above.

Our present conception of alloys is that they may consist of:

1. Similar crystals of one metal.
2. Mixed crystals of different metals.
3. Chemical compounds of different metals.
4. Eutectics of different metals.
5. Mixtures of the above.

The kinetic theory of matter states that matter is made up of molecules and molecular spaces. The molecules are in a state of constant motion. There are two factors at work upon the molecules: molecular motion and the force which tends to bind the molecules together—cohesion or adhesion.

By a simple study of these forces the various physical properties of a metal or alloy may readily be explained.

The physical state of a metal or alloy depends upon the balance between these forces. When a metal is heated, the movement of the molecules is increased, and when the two forces become equal, viz., the force of cohesion and

free movement of the molecules, the metal becomes a liquid or fuses.

It requires heat energy to produce this change, and as the temperature of a substance is the "external evidence of internal molecular motion," then the average velocity of the molecules will determine the temperature of the substance. In the change from the solid to the liquid state the velocity of the molecules must be increased, and so long as the substance remains a liquid at a constant temperature this velocity is constant. It requires a considerable quantity of heat to change a solid substance at the temperature of its melting point to a liquid with an equal temperature. To illustrate: Ice at 0° C. requires 80 units of heat to convert it to water at 0° C.

When a metal or alloy passes from the solid to the liquid state a quantity of heat is taken up, so-called "latent heat," as energy of the molecule, and when passing from the liquid to the solid condition this same quantity of heat is given off.

The following numbers have been obtained for the latent heats of fusion of the substances specified:

	Calories.		Calories.
Water	80.00	Cadmium	13.66
Zinc	28.13	Bismuth	12.64
Platinum	27.18	Lead	5.37
Silver	21.07	Mercury	2.83
Tin	14.25		

ALLOYS OF TWO METALS.

Absolute Immiscibility.—If two metals are alloyed, which are not miscible, they will separate according to their specific gravities, and upon solidifying it will be found that the lower portion of the mass will be made up of crystals of the metal having the greatest specific gravity, while the upper portion of crystals of the lighter metal.

Mixed Metals.—When two metals of different fusing points are alloyed, and the force of adhesion of the molecules is greater than the force of cohesion—*i. e.*, the attraction of the

molecules of a metal for themselves is less than their attraction for the molecules of the other metal—a condition exists in which we have a mixture of crystals. The mixed crystals begin to form at a temperature lower than that of the highest fusing metal. In some cases lower than the lowest fusing constituent metal. The alloy is said to be a “solid solution” and is homogeneous in appearance.

Chemical Compounds.—Two metals may be brought together, and as a result they unite chemically, giving a metallic compound possessing entirely different physical properties. There has been a union between the atoms of the metals, and the crystalline form of this compound is entirely different from that of the component metals. The force which binds them together is entirely different from cohesion and adhesion, but the force of cohesion now binds the newly formed molecules together, and when the alloy crystallizes it will contain one variety of crystals throughout.

Eutectics.—A eutectic may be defined as that mixture in an alloy that has a definite melting point lower than the constituent metals and is of uniform crystalline structure.

A fused alloy containing two metals, A and B, is cooled; that quantity of A or B will separate out, which is in excess, in respect to a mixture consisting of A and B in definite quantities. This continues with the fall of temperature until a certain point is reached; at this point the mixture AB separates out at the same time and in such proportions that the melting point and the composition of the liquid remain unchanged. This mixture behaves like a simple substance, for it exhibits a constant melting point, although it is only a mixture. This mixture is called a *eutectic* mixture. This term eutectics is not limited to alloys, and the same condition is met with in solutions of non-metallic substances. The philosophy of eutectics may be explained as follows: The two metals are soluble in each other to a certain extent, that is, the force of adhesion between the different molecules is greater than cohesion; as the result of this, mixed crystals will be formed, made up to the extent of their solubility. This result is the formation of a mixture having a different

intermolecular force: Between these molecules there is a uniform condition entirely different from that existing between the molecules of the constituent metals. It requires less heat to overcome this adhesive force than it does to overcome the cohesion of the molecules of the free metals. This explains why eutectics have a lower melting point than the constituent metals.

The more metals present in an alloy, the more possibilities in regard to the formation of eutectics; for example, in the case of an alloy containing three metals, A, B, C; A and B, B and C, and A and C may form eutectics possessing the characteristics as to melting point and crystal formation.

Hardness and Fusibility.—It is often found that the metals do not possess sufficient hardness for commercial purposes.

Alloying, as a rule, increase the hardness of metals. Gold and silver both being too soft for the purpose of coinage, when alloyed with about 10 per cent. copper attain hardness sufficient to withstand attrition to the degree required for currency. Tin and copper are alloyed, forming bronze, which is much harder than either of the two metals. In the proportion of 94 parts copper and 6 parts of tin an alloy is produced which is so brittle that it may be broken with a hammer. Antimony and bismuth are noted for their property of imparting hardness to their alloys. In fact, most of the alloys containing an appreciable quantity of either of these metals are brittle.

Copper and silver are added to gold to increase elasticity, and the hardness of gold which *per se* is too soft to be used in the construction of gold bases and in crown and bridge-work.

The fusing point of an alloy is always less than that of the least fusible constituent, but in quite a number of cases it is less than the lowest fusing constituent. In some cases the alloy may have its fusing point at a temperature considerably decreased. Bismuth, cadmium and tin are noted for their ability to depress the fusing points of their alloys, and there are combinations of these metals which fuse at a temperature

less than the boiling point of water, although tin, the lowest fusing constituent, fuses at 232° C. An alloy composed of 5 parts bismuth, 3 parts lead and 2 of tin melts at 91° C., and the addition of small quantities of cadmium further reduces the fusing point to 60° C. This fact is made use of in the construction of solders. The metal to be soldered is alloyed, giving an alloy with a fusing point less than the piece to be soldered. The metallic surfaces may then be united by using this lower fusing alloy without danger of fusing the metallic surface, which would result in ruining the piece. To illustrate: a gold solder for prosthetic work should fuse at a temperature lower than the plate upon which it is to be used. Such a solder should also possess the following properties in order to fulfil all the requirements demanded of it:

(a) Color, which should be as near that of the plate as possible.

(b) Resistance to the actions of the fluids of the mouth.

(c) Ready flow during the act of soldering.

Density.—The density of an alloy is dependent upon the change which takes place in the metals during the act of alloying.

The volume of an alloy may be:

(a) Equal to the sums of the volumes of the constituent metals.

(b) Less than the sum of the volumes of the metals.

(c) Greater than the sum of the volumes.

Consequently an alloy may expand, contract, or neither expand nor contract upon setting. The density will then be governed by (a), (b), or (c) as $\text{density} = \frac{\text{mass}}{\text{volume}}$, i. e., density equals the weight of the alloy divided by its volume.

Alloying may change the volume of the metals, consequently the density will be altered. When the volume is equal to the combined volumes of the metals, the density will be a mean of the densities of the admixed metals. When the volume is less than that of the combined volumes of the metals (alloy contracts on solidifying), the density will be greater than the mean. If the volume of the alloy is greater

(alloy expands), the density will then be less than the mean of the densities of the alloyed metals.

Alloys possessing a greater specific gravity than the mean of their components.

Gold and zinc.
 " tin.
 " bismuth.
 " antimony.
 " cobalt.
 Silver and zinc.
 " lead.
 " tin.
 " bismuth.
 " antimony.
 Copper and zinc.
 " tin.
 " palladium.
 " bismuth.
 " antimony.
 Lead and bismuth.
 " antimony.
 Platinum and molybdenum.
 Palladium and bismuth.

Alloys having a specific gravity inferior to the mean of their components.

Gold and silver.
 " iron.
 " lead.
 " copper.
 " iridium.
 " nickel.
 Silver and copper.
 Copper and lead.
 Iron and bismuth.
 " antimony.
 " lead.
 Tin and lead.
 " palladium.
 " antimony.
 Nickel and arsenic.
 Zinc and antimony.

Color.—The color of an alloy is generally that of the predominating metal. However, in some cases the alloy may have its color completely changed. Three conditions are possible:

1. It may take the color of the predominating metal.
2. It may take the color of a metal which does not predominate.
3. It may take a color entirely different from any of its components.

Malleability, Ductility and Tenacity.—Malleability and ductility are diminished by alloying; the brittle metals in most cases completely destroy these properties when alloyed with even the most malleable and ductile of metals. In the cases of two malleable metals, the resulting alloy is less malleable than either. Example: gold and lead, or lead and platinum. According to Mr. Makins, antimony, when added to gold to the extent of $\frac{1}{1900}$ parts will make gold unworkable.

Tenacity is generally increased by alloying. The following results were obtained by Matthiesen, by employing wires of the same gauge and noting the weights which caused their rupture before and after alloying:

	Pounds.		Pounds.
Copper, unalloyed,	25 to 30;	alloyed with 12 per cent. tin,	80 to 90
Tin, unalloyed,	under 7;	12 " copper,	7
Lead, unalloyed,	" 7;	" tin,	7
Gold, unalloyed,	20 to 25;	" copper,	70
Silver, unalloyed,	45 to 50;	" platinum,	75 to 80
Platinum, unalloyed	45 to 50;		
Iron, unalloyed,	80 to 90;	steel (iron alloyed with carbon) above	200

COMPOSITION OF ALLOYS.

Chemical Compounds.—Staigmüller calls attention to the "periodic law" in grouping those metals which form compounds with each other upon alloying. This classification divides the elements into seven distinct groups, arranged horizontally. The elements composing any vertical column do not form compounds with one another. An element forms compounds with all members of one of the groups or none. Lead, an exception to this, forms two chemical compounds with gold, but none with silver or copper. The following is an abbreviated list of these series:

Li		Mg		Al	Ge	As
	Cu		Zn			
Na		Ca			Sn	Sb
	Ag		Cd			
K		Ba			Pb	Bi
	Au		Hg			

The following is a list of some of the better known commercial alloys and their approximate composition:

Gold coin	{	Gold	90.0
		Copper	10.0
Silver coin	{	Silver	90.0
		Copper	10.0
German silver	{	Copper	50.0
		Zinc	25.0
		Nickel	25.0
Type metal	{	Lead	80.0
		Antimony	20.0

Pewter	{	Tin	92.0
		Lead	8.0
Plumber's solder	{	Tin	67.0
		Lead	33.0
Mellottes (Newton's alloy)	{	Bismuth	8.0
		Lead	5.0
		Tin	3.0
Brass	{	Copper	67 to 72.0
		Zinc	28 to 33.0
Babbit metal	{	Tin	8 to 70.0
		Antimony	2 to 17.5
		Copper	1 to 11.5
Dental alloy	{	Silver	75.0
		Platinum	25.0
Dorrance's alloy	{	Copper	6.0
		Silver	2.0
		Zinc	4.0
Platinoid ¹	{	Copper	60.0
		Zinc	24.0
		Nickel	14.0
		Tungsten	2.0

Decomposition.—The metals composing an alloy are more easily acted upon by acids than the pure metals. Platinum is insoluble in nitric acid, but silver-platinum alloys, containing up to 10 per cent. of platinum, are soluble in nitric acid.

The metals, as a rule, are more readily oxidized in the alloyed condition. Mercury and aluminum undergo decomposition with the liberation of metallic mercury and an oxide of aluminum; the same phenomenon takes place in case of iron and mercury. Noble metals alloyed with base metals, when heated, cause the oxidation of the base metal and by adding a flux the base metal oxides, combines with the flux and is thus separated from the noble metal.

Influence of Constituent Metals.—Mercury, bismuth, tin and cadmium give fusibility to alloys; tin also gives hardness and tenacity; lead and iron give hardness; arsenic, antimony and bismuth render alloys brittle; antimony and bismuth overcome contraction.

Phosphorus and arsenic when added to alloys of copper and tin, have the power of dioxidizing or eliminating metallic oxides which are invariably present. Phosphor-bronze owes

¹ Hepburn.

its closeness of grain and superior tenacity to the addition of phosphorus, and it is claimed "when arsenic or arsenical compounds are made to unite, under suitable conditions, with alloys of copper and tin, known as bronze or gun-metal, it imparts to them several remarkable properties, such as homogeneity, hardness, elasticity, tensile strength and toughness, and a peculiar smoothness, rendering it a valuable antifriction metal for journal bearings," etc.

Manganese and its compounds have a faculty of freeing iron of impurities, the presence of which would render the iron unfit for the manufacture of steel.

Arsenic when added to lead increases the hardness and the fluidity of the molten lead. Advantage is taken of this fact in the manufacture of shot.

Aluminum is a rather hard metal to cast, but when a small quantity of zinc is added the alloy more readily takes up the fine lines of the mold.

Liquation may be described as the separation of a portion of the metals of an alloy, during the act of fusing, into new compounds. When an alloy is heated slowly to a temperature slightly above its fusing point, and is not disturbed, the metals may separate, forming new compounds which have a different fusing point. The newly formed compound will crystallize and if the alloy is again allowed to solidify it will be found that it is not uniform in construction; some portions will contain the newly formed compound and other portions will be of entirely different composition or crystalline form. The result will be that of a heterogeneous mass possessing different properties from the original alloy. Silver and copper alloys possess the tendency of liquating; the copper separates and crystallizes at the edges as the fused mass assumes a solid form. To overcome liquation, an alloy should be thoroughly stirred before pouring. A green stick is sometimes used by plunging it into the molten mass and thoroughly stirring, so as to break up these crystalline formations.

Annealing.—Annealing is the process of heating a metallic substance to restore its original working properties. When a

metal or an alloy is worked, *i. e.*, rolled, hammered or drawn into wire, it becomes harsh. During the mechanical treatment, the molecules of the metal are caused to assume different positions in regard to one another. If the metal is then heated, the molecules are released from this strained condition and, upon cooling, assume their normal molecular relations. Most metals may be annealed by simply heating to a temperature short of their fusing point. Gold, copper and brass are annealed by heating to redness; platinum requires a white heat in order to have its original softness restored. Aluminum is generally annealed by coating it with sweet oil or vaseline and then burning the oily material from its surface. Lead, tin and zinc are best annealed by placing them in boiling water and allowing them to cool slowly.

Temper.—When steel is heated and suddenly chilled a peculiar condition results; instead of the metal becoming soft it acquires an unnatural degree of hardness and is said to be tempered.

The hardening of iron with carbon (steel) is generally understood to mean the heating of the metal to a high temperature and then plunging it into a bath for the purpose of suddenly cooling it. While this is true of most steels, a few alloying materials now used reverse this, the hardest and toughest state being obtained by slow cooling in the air.

By quenching steels from high temperatures and tempering, their wearing qualities, elastic limits, tensile strength, magnetic qualities, and resistance to shock can be greatly improved, and yet they will not be so hard that they cannot be scratched with a file.

The factors having an influence upon the hardness are the nature and composition of the metal, the temperature of the metal when quenched, volume and temperature of quenching bath.

High temperature causes a rearrangement of molecules and a change in chemical composition; sudden cooling holds the molecules in this changed position.

The temperature necessary to bring about the intra-

molecular changes depends upon the variety of ingredients which have been alloyed with the steel.

By polishing the surfaces of steels which have been quenched at different temperatures, and then etching these surfaces with picric or hydrofluoric acid a very characteristic configuration can be seen with the aid of the microscope. These appearances in steels of different kinds and tempers are due to the separation or combination of definite chemical compounds. These compounds are respectively known as ferrite (pure iron); cemetite (iron carbide); pearlite (intimate mixture of ferrite 32 parts and cemetite 5 parts); martensite (appearing as fine intersecting lines in steel containing 0.85 per cent. carbon and which has been heated to 1400° F., before quenching); austenite (in steel containing 1.1 per cent. carbon, suddenly cooled from 2000° F.). Troostite and sorbite are other forms.

In subjecting steel to different heat treatments we can change the constituents from pearlite to martensite, sorbite, austenite and troostite, and back again through these different stages, and by examining them with the microscope we can judge very closely the treatments to which they have been subjected. As these changes cause the constitution, static strength and dynamic properties to change, we can easily see the importance of this knowledge.

Preparation.—The process of alloying metals is rather complex, and before any attempt is made to produce an alloy, the physical properties of the metals to be alloyed should be thoroughly studied.

During the heating process, base metals should be melted in a suitable vessel, and the flame should not come in contact with the metallic surfaces.

Noble metals may be alloyed with base metals in two ways: (1) Melting the higher fusing noble metals and protecting the surface by a suitable flux; then quickly plunging the base metal below the surface of the molten mass. Some metals as zinc, cadmium and antimony, when alloyed with metals which have a much higher fusing point, may be more readily alloyed by wrapping them in paper

and then plunging below the surface of the molten mass of the higher fusing metals. (2) The base metals may be fused first, then the noble metal in the form of a thin ribbon may be slowly added. An alloy consisting of tin and silver can be prepared by fusing the tin (M. P. 232° C.), and then adding the silver (M. P. 960° C.) in the form of a very thin ribbon. The advantage of this method is that there is less danger of oxidation of the base metals. This would be lost from the alloy. To insure a uniform mix, it is always best to fuse a freshly prepared alloy a second time and to thoroughly agitate the mass before pouring.

Granulating-pouring the alloy from a height into a vessel of water, or rolling out the alloy, before the second fusion, will assist in obtaining an intimate mixture. Base metal alloys may have the dross (oxides), which forms on their surfaces during fusion, reduced by placing a hydrocarbon in the retort while the alloy is still in the fused condition.

To prevent occlusion of gases by fused alloys, a specially constructed furnace must be used. Some inert gas like nitrogen is forced into the furnace, driving out the oxygen of the air and thus preventing occlusion. Some metals when heated to their fusing point oxidize so readily that it is very difficult to obtain the metal in a fused condition necessary for alloying. The same form of furnace is used in this case as described above.

It is sometimes necessary to have a substance present that will prevent the oxidation of the metals during fusion. This forms a protecting layer and prevents the oxygen of the air from coming in contact with the metallic surfaces.

For *high* fusing metals fused borax or salt is commonly used. For *low* fusing metals powdered charcoal, graphite or hydrocarbons are made use of.

Pouring of Fused Alloys.—The proper degree of heat at which an alloy should be poured is that temperature just above its fusing point, when it will pour readily. In pouring into a mold, if the metal be poured at a temperature too much above its fusing point, the cooling mass will contract until the temperature of the room is reached, thus causing

an undue amount of contraction; on the other hand, if it is poured at a temperature too low, the alloy does not possess sufficient fluidity to take up the fine lines of the mold. With base metals, as lead and zinc, the degree of heat for pouring may be roughly estimated by plunging a green stick into the molten mass; if there is no vibration felt, the metal is in a proper condition to be poured.

CHAPTER V.

METALLURGICAL APPARATUS.

THE fuels used in metallurgical operations depend upon (a) their cost; (b) their availability; (c) the nature of the operation.

The unit of heat value is called the calorie. A calorie (small c) is the quantity of heat necessary to raise the temperature of 1 gram of water one centigrade degree. A Calorie (large C) is 1000 times *small c*, or the heat necessary to raise 1000 grams of water 1 degree.

The value of a fuel is measured by its caloric value. In reductions as practised in smelting works, coal, oil and producer gas are the principal fuels. Coal is dependent upon carbon and hydrogen compounds of carbon for its calorific value. Oil consists of a complex mixture of hydrocarbons. The oil is mixed with steam and forced into a furnace, called an oil ejector furnace; intense heat results. Many industries are taking advantage of this form of fuel, especially when intense heat is required.

Producer Gas.—This gas is produced by the incomplete oxidation of coal. In its preparation the caloric value is considerably lessened; consequently this form of fuel is not so economical as some of the others.

Fuels Used in Dental Metallurgy.—The fuels used in dentistry may be enumerated as follows:

- | | | |
|-----------------|--------------------------------------|------------------------|
| (a) Liquids | { Petroleum
Alcohol
Hydrogen | { Coal oil
Gasoline |
| (b) Gases | { Coal gas
Water gas
Acetylene | |
| (c) Electricity | | |

Coal Gas.—Coal gas or water gas is the principal fuel used by the dentist. Coal gas is the product of the destructive distillation of coal, and is made up of hydrocarbons. Water gas is prepared by passing steam over heated coke, causing a decomposition of the water, and the formation of a mixture of hydrogen and carbon monoxide; both of these gases burn with a non-luminous flame, and to make them luminous, so that the gas may also be used for illuminating, oil is cracked into the gases. The carbon monoxide and hydrogen are passed through a chamber filled with bricks heated to a bright redness, the oil is allowed to enter and a decomposition takes place, resulting in the formation of gaseous hydrocarbons. The composition of the finished product consists of carbon monoxide, hydrogen and gaseous hydrocarbons.

Natural gas requires specially constructed blow-pipes in order to obtain the greatest efficiency in its use. Coal oil and gasoline for blow-pipe work are vaporized. In using gasoline every precaution should be taken to prevent the reservoir tank from coming in close proximity with the blow-pipe or a free flame, as many accidents have resulted from this.

Hydrogen with oxygen is used to obtain high temperatures in the oxyhydrogen blow-pipe for melting platinum and also in cast gold work. Acetylene with oxygen and also air is used when gas is not available, and seems to serve as a very good substitute.

Electricity may be used in two ways: (a) By passing it through a substance which offers resistance and advantage taken of the heat produced. The electric furnace for porcelain work is an illustration of this method. (b) By forming an arc, which produces intense heat; this is used in melting the most refractory metals.

Electricity is also used for various other metallurgical purposes, *i. e.*, (a) depositing metals from solution (electroplating); (b) as a power to run motors, for lathes, compressed-air machines, etc.

Furnaces.—*Coal Furnaces.*—These are of two types, depending upon the nature of the current of air used in the combustion of the fuel:

(a) *Chimney draft*, in which the natural air draft from a chimney is used. Reverboratory, open hearth, and the small furnaces usually used for melting base metals, are of this type.

(b) *Forced Draft or Blast Furnace*.—In this type of furnace an artificial current of air is produced to accelerate the combustion of the fuel. The blast furnace as described under Iron, is a type of this variety of furnace.

HEATING DEVICES.

Alcohol.—Alcohol blow-pipes are useful when gas is not available. Fig. 18 illustrates this form of blow-pipe. Wood or denatured alcohol may be used, and a needle-pointed flame of remarkably high temperature will result. The double-jet construction of the burner generates the maximum degree of heat from the fuel, over 1600°C . (3000°F .). The flame is perfectly clean and non-oxidizing. The burner is swiveled so that it can be turned in any position.

Gasoline.—In Fig. 19 we have a very convenient form of gasoline lamp for melting base metals. The stand may be used for holding the melting pot or other objects to be heated. Fig. 20 represents the familiar form of gasoline torch, fitted with a holder so that it may also be used for heating objects. The torch may be released from the stand and also be used for soldering purposes.

Gas Burner, etc.—The familiar Bunsen burner will not require a description; however, a word or two in regard to the nature of the flame may not be amiss. A flame may be considered a mass of highly heated gases, undergoing rapid combustion. The Bunsen-burner flame is made up of three cones: (1) consisting of a mixture of combustible gases; (2) consisting of gases in which combustion is starting; because of the nature of this cone, being low in oxygen, it is called the reducing flame, abbreviated R. F.; (3) consisting of gases in which combustion is completed; there is sufficient oxygen present to completely oxidize the combustible gases. This flame is called the oxidizing flame (O. F.).

To increase the rate of combustion, which would result in also raising the temperature of the flame, a blast is made use



FIG. 18.—Blow-pipe for alcohol.
(Central Scientific Company.)



FIG. 19.—Blast lamp, gasoline,
"Dangler's lamp."
(Central Scientific Company.)

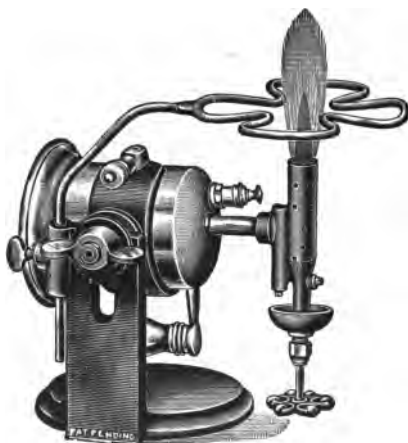


FIG. 20.—Adjustable laboratory blast lamp, fitted with adjustable stand and tripod. (Central Scientific Company.)

of. The blow-pipe in its simplest form is used by a blast from the mouth. The large end of the instrument is held between the lips and the small end toward the flame. The blast should not be sustained by the respiratory organs, but, in order that an unbroken current may be kept up, the mouth should be filled with air, to be forced through the blow-pipe

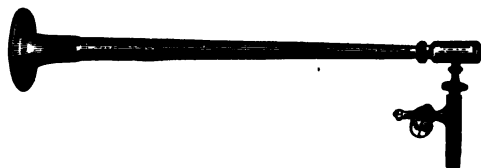


FIG. 21

by the muscles of the cheeks. While these are forcing the air through the blow-pipe, the connection between the chest and the cavity of the mouth should be closed by the palate, which thus performs the part of a valve. The beginner is liable to fall into the error of not closing the connection between the chest and the mouth at the proper instant, so as to obtain the force necessary to propel the air through the blow-pipe from the lungs. To avoid tiring the muscles of the

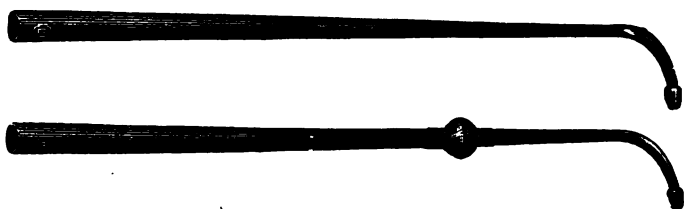


FIG. 22

lips by continual blowing, the trumpet mouth-piece has been recommended (Figs. 21 and 22). This is merely pressed against the open mouth, and an uninterrupted blast may be kept up for a long time without causing fatigue of the orbicularis oris, since that muscle takes but a passing part in the operation.

The blow-pipe should be constructed of either brass or German silver, as these alloys are but poor conductors of heat.

A long-continued and steady flame maintained by the mouth blow-pipe is apt to cause a disturbance in the flame from the collection of moisture in the tube, which is liable



Fig. 23

to be expelled by the pressure of the air. To avoid this, a hollow chamber is constructed about midway in the instrument. Fig. 23 illustrates another type of blow-pipe, usually connected with a bellows for the furnishing of the air blast;

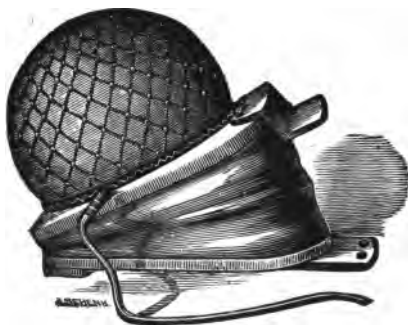


FIG. 24

Fig. 24 is the usual form of bellows used in dental metallurgical operations.

Compressed air, furnished by electric switchboards, is the common form of blast that is being used at the present time, and the up-to-date office buildings are also prepared to furnish compressed air to their patrons.

When a small quantity of gold or silver is to be melted by means of the blow-pipe, it is usually performed upon a support of charcoal. A good solid cylindrical piece of thoroughly charred pine coal should be selected, and divided into two equal halves by a vertical cut with a saw. Upon the end of one-half, a depression should be cut for the reception of the metal to be melted. On the flat side of the other half, extending to the end, the ingot mold should be carved, of size and shape governed by the requirements of the case. The two halves should then be brought together and secured by a piece of iron or copper wire, when they will be found to practically combine the requirements of crucible and ingot mold. The depression in which the metal is to be melted and the mold or receptacle should be connected by means of a gutter or groove. The flame is now directed upon the metal, and when thoroughly fluid, the charcoal is tilted so that the fused metal will run into the mold prepared for it in the opposite half of the charcoal. This is probably the simplest form of apparatus by which small quantities of metal can be melted, and is often employed in the dental laboratory and by jewellers.

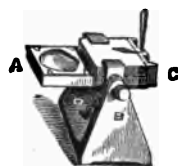


FIG. 25

Fletcher has devised an apparatus embodying the same general principles as the one just described for quickly obtaining ingots of gold and silver without the use of a furnace. It is shown in the accompanying diagram (Fig. 25); *A*, representing a crucible of molded carbon, supported in position by an iron side-plate; *C*, the ingot mold; *B*, clamp, holding ingot mold and crucible in position; *D*, cast-iron stand upon which the latter swivels. The metal to be melted is placed in the crucible *A*, and the flame of the blow-pipe directed upon it until it is perfectly fused. The waste heat serves to make the ingot mold hot. The whole is tilted over by means of the upright handle at the back of the mold. A sound ingot may be obtained by the use of this simple little apparatus in a very few minutes. Simple contrivances of this kind are, however, not applicable

to melting operations involving quantities exceeding one ounce. In such cases it is better to employ a crucible and any stove or furnace in which the temperature can be raised sufficiently. This may be accomplished in an ordinary cooking stove, a blacksmith's forge, or a small fire-clay furnace, by the use of anthracite coal, coke, or charcoal.

Fletcher Furnace.—By far the most convenient, compact, and effective furnace for melting from 1 to 10 ounces of gold, which has ever been used, is the crucible furnace (Fig. 26), invented by Mr. Fletcher, which can be obtained at the dental depots. The furnace is perfectly adapted to the wants of the mechanical dentist. It is composed of a substance

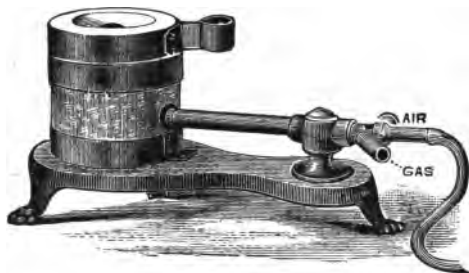


FIG. 26

resembling fire-clay, but much lighter in weight, and said to possess only one-tenth its conducting power for heat.

The furnace consists of a simple pot for holding the crucible, with a lid and a blow-pipe, all mounted on a suitable cast-iron base. As compared with the ordinary gas furnace it appears almost a toy, owing to its great simplicity. The casing holds the heat so perfectly that the most refractory substances can be fused with ease, using a common foot-blower. Half a pound of cast-iron requires from seven to twelve minutes for perfect fusion, the time depending on the gas supply and the pressure of air from the blower. The power which can be obtained is far beyond that required for most purposes, and is limited only by the fusibility of the

crucible and casing. The crucible will hold about ten ounces of gold. An ordinary gas supply-pipe of $\frac{5}{16}$ or $\frac{3}{8}$ inch diameter will work it efficiently. It requires a much smaller supply of gas than any other furnace known; about 10 cubic feet per hour is sufficient for most purposes. Crucibles must not exceed $2\frac{1}{4} \times 2$ inches. Any common blow-pipe bellows will work the furnace satisfactorily, except for very high temperatures (fusion of steel, etc.), for which a very heavy pressure of air is necessary. In size, it is but four inches in diameter by three in height. The author has used one in his laboratory for the purpose of melting gold and silver and for general metallurgical experiments for several years

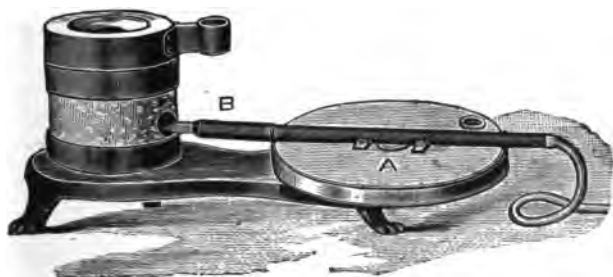


FIG. 27

with the greatest satisfaction; he has also found it to be most admirably adapted to class demonstration, for which purpose, as a means of illustrating his lectures on metallurgy, he has had frequent opportunities to use it.

A modification of the apparatus has been made, adapting it to the use of refined petroleum instead of gas as a fuel, and thus rendering it of more general utility (see Fig. 27). Thus improved, it is said to be in no way inferior in efficiency to the gas furnace. The burner of this furnace is constructed upon the principle of an atomizer, which, of course, dispenses with a wick; it is supplied with a device for regulating the supply of oil, which is operated by the milled nut (marked A) shown on the top of the reservoir in the cut, and for the supply

of an annular jet of air, which is regulated by turning the sleeve (marked *B*). This burner is so arranged that in case any obstruction should occur it can be taken apart and cleaned by separating the burner from the reservoir, which is accomplished by loosening the small screws, drawing out the oil-tube, taking off the sleeve *B*, and removing the inside tube.

These furnaces are so constructed that they may be used for either gas or petroleum, the lamp being fitted for adjustment in place of the gas-burner, so that the same apparatus may be used for either. The blast is obtained by means of the foot-blower shown in Fig. 24, which is connected with the furnace by means of India-rubber tubing, as seen in Fig. 27.



FIG. 28

Muffle Furnace.—Brown's assay furnace (Fig. 28) illustrates this form of furnace; in it coke is used as a fuel. The older furnaces used in continuous gum work were of this type. The muffle used is of a refractory material and during the heating process the metals do not come in contact with the products of combustion. If an alloy of gold and lead is placed in the muffle in a small dish composed of bone

ash, the lead will be oxidized, leaving the gold as a bead. This process is called cupellation; the bone ash dish is the cupel.

The electric muffle furnace consists of a muffle wrapped with platinum wire of about 28-gauge, and then covered with a mixture of refractory materials, such as fire-clay. The muffle is then put into position in the outside casing, which differs in the various makes of furnaces. The platinum-wire



FIG. 29

wrapping leads to binding posts. Then from the binding posts it passes to some form of a resistance coil which regulates the amount of current passing through the furnace. The resistance coil or rheostat gives us control of the temperature. Hoskins' furnace is a good illustration of a furnace in which electricity is made use of for heating purposes. Fig. 29 illustrates this type of furnace. Chromel, a nickel-chromium alloy, is used instead of platinum.

The electric furnaces used in porcelain work, of which

there are many types in use, as a rule contain platinum wire and serve to illustrate an electric muffle furnace.

Refractory Materials.—Refractory agents are those that can withstand the agency of heat without destruction. The ideal refractory material should not decompose or crack upon sudden changes of temperature, nor be attacked by the metal or flux used during the heating process. They are used: (a) In the construction of furnaces. Example: fire-clay. (b) To construct crucibles or other receptacles for melting metals. Examples: fire-clay, graphite, charcoal, asbestos, etc. (c) To line furnaces and crucibles. Examples: oxide of iron, magnesium oxide, etc. (d) To act as a support for metallic pieces during soldering or casting. Examples: investing compounds of various compositions.

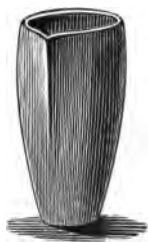


FIG. 30



FIG. 31

Crucibles.—The term “crucible” is applied to a chemist’s melting pot (Figs. 30 and 31), made of earthenware or other material, and so-called from the superstitious habit of the alchemists of marking such vessels with the sign of the cross. The term is now generally understood as designating vessels in which metals are melted in furnaces at high temperatures. A crucible should possess the power of resisting high temperatures without fusing or softening. It should also be capable of retaining sufficient strength, when hot, to prevent its crumbling or breaking when grasped by the tongs. Lastly, it should not crack either in heating or cooling.

For the purpose of melting metals, crucibles are made of

clay with admixture of silica, burnt clay, graphite, or other infusible material. For the fusing of platinum, which requires the intense heat of the oxhydrogen flame, they are formed of lime. For use in the dental laboratory, graphite crucibles, which can be obtained at the dental depots, will be found to answer every purpose, and they are thoroughly reliable in strength and durability. They range in size from 2 to 4 inches high. When the quantity of metal to be melted is very small, say a half-ounce of gold, the smallest-sized Hessian crucible may be used in the small Fletcher apparatus. Crucibles suitable for melting platinum or iridium are formed of two blocks of lime, each block having a concavity or excavation, so that when the two pieces are placed together the center is hollow; it is thus designed to hold the scraps of platinum to be melted. The lower block is also arranged with a groove and lip, so that when the metal becomes fluid it may be poured into a suitable ingot mold by inverting the crucible. The compound flame is introduced by tubes passing through the center of the upper block of lime forming the cover.

Before melting any considerable quantity of gold, the crucible should be tested, particularly if the melting operation is to be performed in an ordinary coal stove, where a defective crucible might be the means of a considerable loss. A small amount of borax should be placed in the vessel, which should then be exposed to a high temperature. Should it not be perfect, the borax glass will run through and glaze the surface on the outside. If the crucible is found to be impervious it should be so inverted, while yet hot, that the borax glass may cover the surface of the lip or groove out of which the melted metal is to be poured. This facilitates the pouring and prevents any portion of the metal from adhering to the side of the crucible.

Scorifiers (Fig. 32).—Scorifiers are small dishes from 2 to 3 inches in diameter and about 1 inch deep. They are made of a refractory fire-clay, like crucibles, and should not be too deep, as the object is to expose the largest possible surface of molten lead to the air current.

Roasting Dishes.—Roasting dishes are similar to scorifiers, except that they are a little more shallow and much wider.

Cupels.—Cupels, as the name indicates, are small, cup-like receptacles. They are made of bone-ash obtained by burning the bones of horses and cattle. It is customary to mix the



FIG. 32.



FIG. 33

pulverized bone-ash with 1.5 to 2 per cent. of fire-clay and with a little water, just enough to make it stick together without making it appear wet. This is then packed into a suitable mold and compressed by means of a die. The cupel is then removed from the mold and allowed to become

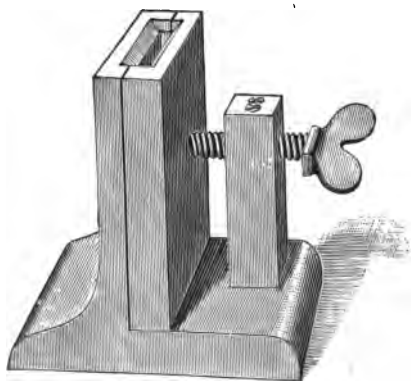


FIG. 34

thoroughly dry in the air, and finally calcined to expel all moisture and to decompose any organic matter which might be present in the form of splinters of wood, small pieces of paper or other impurities. If this calcinating were not done, the gases arising when first heated would cause a spattering

of the molten lead and a consequent loss of noble metal in the assay.

Scorification Molds (Fig. 33).—These are used for pouring the assay charge. The conical shape is preferable to the old-fashioned flat style.

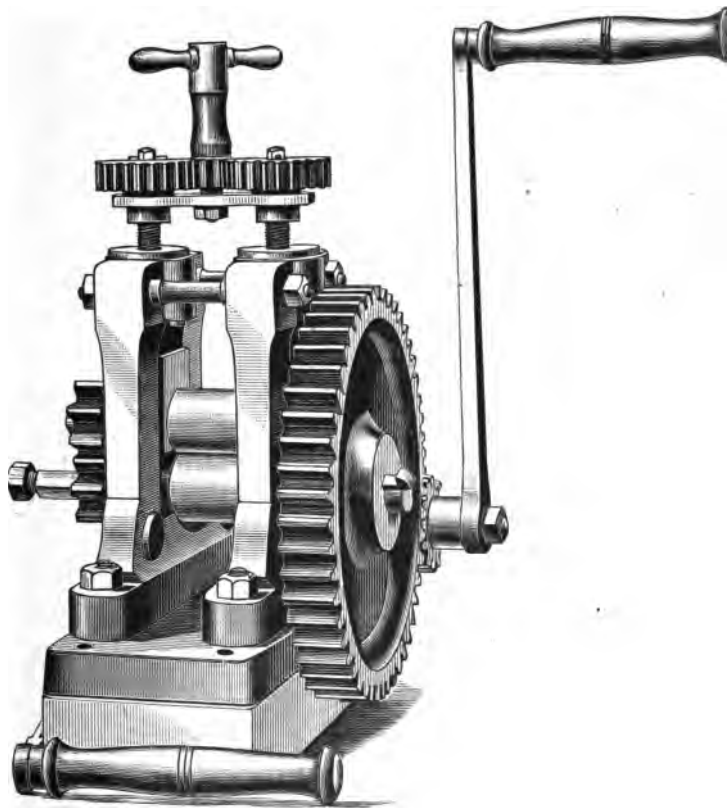


FIG. 35.

Ingot Molds.—Ingot molds are constructed of various substances. For the reception of platinum melted with the

oxyhydrogen blow-pipe they are formed of lime or coke; for gold and silver they are commonly made of cast-iron, about 2 inches square and from $\frac{1}{8}$ to $\frac{3}{16}$ inch in thickness (Fig. 34), with slightly concave inner surfaces, as the shrinkage of the ingot is greatest at the center. Ingot molds formed of soap-stones are also employed. The ingot mold should be heated before pouring.

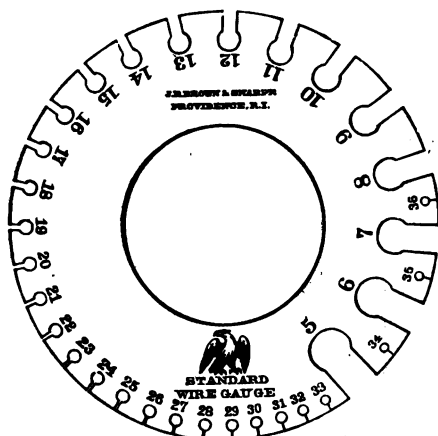


FIG. 36

The Rolling Mill.—Rolling or laminating is accomplished by repeatedly passing the metallic ingot between cylindrical steel rollers from 3 to 4 inches in width. These are so arranged that by means of screws, they are capable of being brought closer together every time the gold is passed through (Fig. 35). The proper degree of attenuation is determined by the gauge-plate (Fig. 36).

Draw-plate (Fig. 37).—Gold or silver is made into wire by means of the draw-plate—an oblong piece of steel provided with a number of gradually diminishing holes enlarged on the side where the gold enters. The gold to be drawn through may be prepared in a cylindrical shape by melting and

pouring into an ingot mold provided with a chamber for the purpose (some ingot molds are so constructed). The end of the rod should be filed so as to readily enter the draw-plate, which must be firmly screwed in a vise. The gold is then, by means of a pair of strong pliers, drawn through the different holes of the draw-plates consecutively until the desired size is reached. At the beginning of the operation it will require frequent annealing.



FIG. 37

INSTRUMENTS AND METHODS OF DETERMINING PHYSICAL PROPERTIES OF METALLIC SUBSTANCES.

Specific Gravity.—The chemical balance (Fig. 38) is used in weighing the object in air, and then a small platform is placed over the pan of the balance; a beaker of water is then placed on the platform; the difference in weight in air and in water is the weight of an equal volume of water. The specific gravity of a substance will then be represented by the following:

Sp. gr. = $\frac{W}{W - W'}$, when W is the weight in air, and W' equals weight in water.

Temperature.—Mercury thermometers are used for temperatures as high as 360° C.; above this temperature mercury boils, and some other device must be used.

Low fusing metals or alloys may be fused in a "Jena" glass flask, placed upon a sand-bath to insure uniform heating of the flask. Care must be taken not to let the thermometer touch the sides of the glass, or a false reading of the temperature will result. Crucibles or hard test-tubes

may also be used instead of the Jena flask. For high temperatures, pyrometers must be used. The name pyrometer is given to those instruments for measuring temperatures so high that mercurial thermometers could not be used. The three principles upon which pyrometers are constructed are:

1. The expansion of gases and vapors.
2. The specific heat of solids.
3. The electric properties of bodies.

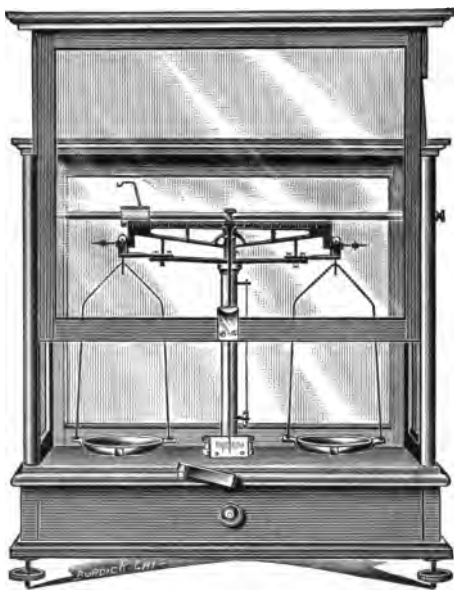


FIG. 38

Pyrometers of the third group are the only ones that need to be described; information on the first two classes may be found in any book on physics.

If two metals are soldered together, their extremities joined in a metallic circuit and the junction between them heated, an electric current is produced. This was called a thermo-electric current. The thermo-electric motive force is dependent upon the temperature. A thermojunction of

palladium and platinum wires was used by Becquerel for measuring the temperature of a furnace. The wires were firmly tied together by platinum wire for a distance of 1 cm. at one end. This junction was placed in the region the temperature of which was required; the wires being protected by a porcelain tube, and their outer ends soldered to copper wires in circuit with a sensitive galvanometer. The junction is placed in a vessel of melting ice so that the two metals being at the same temperature, could not give rise to any thermo (E. M. F.). The galvanometer deflection is pro-

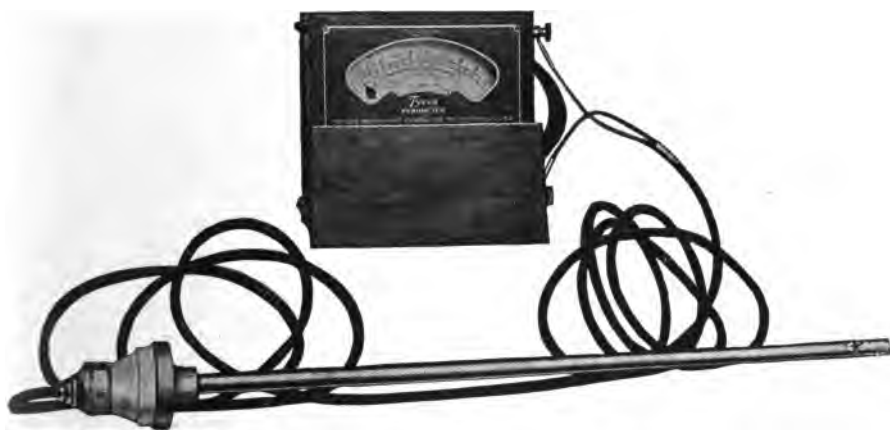


FIG. 39

portional to the temperature of the furnace and the instrument is first standardized by being placed into various substances at their known melting point. This explains the principle of the pyrometer of the third class, as originally worked out. In Fig. 39 we have a pyrometer consisting of a thermo couple and a temperature indicator. The fusing point of brass, bronze, lead, and zinc may be readily determined with this instrument. The maker guarantees this instrument accurate up to a temperature of 1200°C . and may be used to indicate a temperature as high as 1400°C .

Linear Expansion.—Linear expansion is determined by the expansion of a rod of the metal during a given range of temperature. Fig. 40 represents an apparatus for determining the linear expansion of a bar of metal. The apparatus consists of a water jacket, a binding screw, place for a thermometer; at the opposite end to the binding post there is a lever attached to a pointer; also a graduated scale or dial to record results. The metallic rod is placed in position within the steam jacket, and the set screw is regulated; the thermometer is next set into place. Cold water is run through the water jacket and the temperature reduced to zero degrees if possible; in the most exact determinations with more complicated apparatus, this is necessary. The

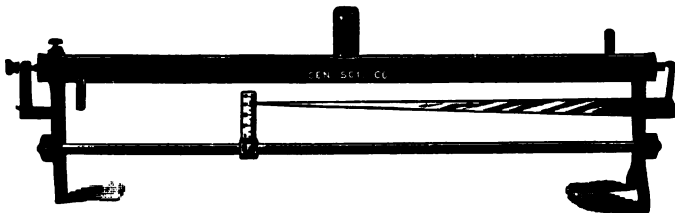


FIG. 40

length of the rod at zero is fixed by means of the set screw and the latter is regulated so that the pointer stands at zero on the scale. The temperature of the water is gradually changed, and finally steam is passed through the water jacket until the thermometer registers 100° . The dial, which registers the elongation produced, is read and the amount of expansion per degree per cubic centimeter is calculated.

Conductivity of Heat.—Two similar bars of metal are placed end to end and heat applied. The temperature of the bars in different places is measured by applying the junction of a thermo-electric couple. Wiedeman and Franz made use of this method of determining the conductivity in the following way: The metal bars were made as regular as possible and were silver-plated and polished so as to have the same radiating power, one of the ends was heated to 100° ,

the rest of the bar being surrounded by air at a constant temperature. The results of their experiments are the figures given in Chapter III.

Specific Heat.—The specific heat of substances may be determined in any of the following ways:

- I. Method of mixtures.
- II. Method of melting ice.
- III. That of cooling.
- IV. By the steam calorimeter.

I. *Method of Mixtures.*—By this method the specific heats of the metals may be determined in the following manner: The substance is weighed and raised to a known temperature by keeping it for some time in a place heated by steam; it is then immersed in a mass of cold water, the weight and temperature of which is known. From the rise of temperature of the water after mixture the specific heat of the body is determined. If a kilogram of water and a kilogram of mercury be each heated to 100° and then poured into a separate kilogram of water at 0°, in the first case the water will raise the temperature of the water to 50°, while the mercury will raise the temperature of water 3.2°. While the water in cooling has raised the temperature of an equal weight of water from 0° to 50°, the amount of heat in a kilogram of mercury at 100° has only raised the temperature of an equal weight of water from 0° to 3.2° and in doing so has itself become lowered in temperature, $100 - 3.2 = 96.8^\circ$. The amount of heat contained, therefore, in equal weights of water and mercury at the same temperature as shown by these figures, is as:

$$\frac{50}{50} : \frac{3.2}{96.8} = 1 : \frac{1}{30} \text{ or } 0.33.$$

II. *Method of Melting Ice.*—This method was devised by Black, the discoverer of specific heat. A cavity is made in a piece of ice to receive the metal to be tested. An ice covering is then made to fit tightly over the cavity to prevent a loss of heat from this source.

The metal is weighed and heated to a given temperature, the cavity in the ice is thoroughly dried—the metal is then

introduced and allowed to remain until it reached the temperature of the ice (0°). The water from the melted ice is collected upon weighed blotting paper or a sponge and again weighed to ascertain the quantity of ice melted. The specific heat is then calculated as follows:

$$\text{Sp. heat} = \frac{\text{Latent heat of ice (80 cal.)} \times \text{weight water.}}{\text{Weight of metal} \times \text{temperature difference of metal.}}$$

When ice passes from the solid to the liquid state it takes up 80 calories of heat (as energy of the molecule) and when the weight of water as determined by this experiment is multiplied by 80, the product represents the number of calories of heat which is given up by the metal in passing through the range of temperature. If this quantity be divided by the weight of the metal times the number of degrees through which the metal has passed, the result will represent the quantity of heat per gram of weight which the metal possessed as compared with water (specific heat).

III. *By Cooling*.—This method is not used in determining the specific heat of metals or other solids; however, it is of service in determinations upon liquids. The method is based upon the fact that substances possessing different specific heats will have their temperatures reduced at a different rate in succeeding units of time. By accurately measuring the rate of fall in temperature, the specific heats of liquids may be determined.

IV. *Steam Calorimeter*.—A known weight of a substance, at a known temperature is placed in a vessel containing steam and again weighed; from the weight of condensed steam upon the object, the quantity of heat which has been required to raise the substance to the given temperature of the vessel is estimated. The latent heat of water being known (607 cal.), then the specific heat may be obtained by the following formula:

$$\text{Sp. heat} = \frac{\text{wt. condensed water} \times 607 \text{ cal.}}{\text{wt. substance} \times (t^1 - t^0)}$$

In this equation t^0 represents the first temperature of the object and t^1 , the temperature to which the object has been raised during the condensation of the steam.

Measure of the Quantity of Heat.—The quantity of heat disengaged during chemical action is measured by means of the calorimeter. Oxidation is the principal chemical action used in obtaining quantities of heat, as in the burning of the various fuels. An instrument is so devised that the heat given off is taken up by a known weight of water, and from this the caloric value is calculated according to the standard established for the calorie, as has been elsewhere stated in this text. The following list gives the heat in calories, disengaged by a gram of each of the substances while burning in oxygen:

Hydrogen . . .	34,462	Coke	7000
Petroleum . . .	11,000	Carbon monoxide .	2400
Anthracite . . .	8,460		

Conductivity of Electricity.—Conductivity of electricity is a term used to refer to a specific property of a material which conducts an electric current through a unit of length and cross-section. The physical condition of a metal and also the temperature at which the determination is made both have an influence upon the conductivity. The table in this text is a comparative one, using the conductivity of silver as 1000. By dividing the absolute unit of resistance represented in microhms of silver by the figure representing the resistance of some other material represented in the same unit, and then multiplying by 1000 the figures used in the table were obtained.

Hardness.—For ordinary purposes the table of comparative hardness may be used. In this table we have ten degrees of hardness; No. 10 will scratch any substance in the scale, while No. 9 will scratch all those below it, but will in turn be scratched by No. 10. The following is the table of comparative hardness:

- | | |
|--------------|----------------|
| 1. Talc, | 6. Orthoclase, |
| 2. Gypsum, | 7. Quartz, |
| 3. Calcite, | 8. Topaz, |
| 4. Fluorite, | 9. Sapphire, |
| 5. Apatite, | 10. Diamond. |
- Corborundum ranks between No. 9 and No. 10.

The table of hardness of metals is as follows:

Lead,
Tin,
Aluminum,
Gold,
Silver,
Platinum,

Zinc,
Copper,
Soft iron,
Mild steel,
Hard cast iron,
Hardened steel.

Hardness of a body has no relation to its resistance to compression. Glass and the diamond are much harder than wood, but the latter offers far greater resistance to the blow of a hammer.

Tenacity.—For measuring the tensile strength of wires, Fig. 41 represents one of the various forms of devices. The

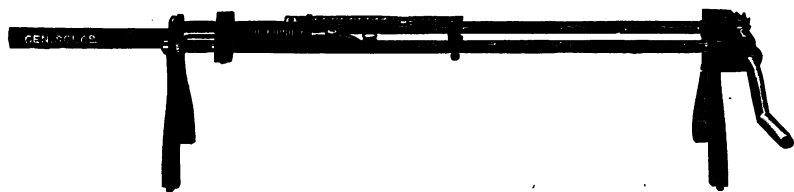


FIG. 41

wire of definite gauge is placed in the machine and force is applied by means of the lever. The machine is fitted with a spring balance for recording the amount of force applied.

Malleability and Ductility.—The figures given are only approximate as there is no means of standardizing these physical properties.

SPECIAL METALLURGICAL OPERATIONS.

Study of an Alloy.—The following is a brief outline as to the method of studying an alloy:

Thermic Analysis.—The metals are alloyed and allowed to cool slowly; the time consumed in the fall of temperature is carefully noted, and recorded. By this means the formation of eutectics may be determined by the arrest in the fall

of temperature. To illustrate: An alloy is heated to, say, 350° and the temperature recorded every ten seconds.¹

Seconds.	Centigrade.	Seconds.	Centigrade.
0	350°	90	202°
10	328	100	188
20	307	110	184
30	287	120	180
40	267	130	180
50	250	140	180
60	238	150	180
70	227	160	169
80	215	170	159

The conclusion drawn from the above chart shows: (1) A primary retardation of cooling, lasting from 250° C. to 180° C., and during this interval a primary crystallization has taken place; (2) The temperature remains stationary for thirty seconds at 180°, indicating a second crystallization at this point. The above is an alloy of lead 65 per cent. and tin 35 per cent. The arrest of the temperature upon cooling is due to crystal formation; the latent heat given off during solidification causes this arrest.

Microscopic Examination.—The metallic substance is highly polished and then etched with some suitable acid. Nitric (dilute or concentrated), picric, or hydrochloric acids, may be used. The object of etching is that it brings out the crystal formation so that it may be more readily seen through the lens. The microscope for this purpose is so constructed that opaque objects may be readily seen; it is fitted with a mirror, so situated that light is reflected to the surface of the metal, which is seen through the eye-piece. The physical properties are studied by the methods already described in this chapter, and finally a quantitative chemical analysis is made to determine the composition; this last step is very important, due to the fact that there may be a change in the proportions of the metals present in an alloy, due to oxidation during alloying.

Soldering.—Soldering must also, to a certain extent, be regarded as coming under the general head of melting opera-

¹ Fenchel.

tions, since it refers to the union of two or more pieces of metal by means of a more fusible alloy. The conditions of successful soldering are: (1) Contact of the two pieces to be united. (2) A clean metallic surface over which the solder is to flow. (3) A freely flowing solder. (4) Proper amount and distribution of heat.

Contact of the pieces to be united is of the greatest importance. If, for example, the object to be soldered be an artificial denture, it is an indispensable requirement that the backings be quite or very nearly in contact with the plate, and, if gum teeth be used, that each backing touch its neighbor. If, however, any defects of this character are found to exist after the teeth have been invested, they should be remedied by filling such spaces or crevices with small pieces of gold or silver, as the case may be, thus rendering the continuity of the parts complete. By the observance of this precaution much of the vexation in soldering experienced by beginners may be avoided, and when the other conditions named have been observed, the operation becomes exceedingly simple. Solder runs freely by the force of capillary attraction between two closely fitting surfaces, just as water will be drawn against gravity between two panes of glass in close contact. The difficulties of soldering are mainly due to a violation of one or more of the rules herein given. Cleanliness should always be strictly observed in soldering operations. The parts to be united should present bright and clean surfaces. Darkening by oxidation will always occur when gold or silver, which has been alloyed with copper or brass, is heated to redness. A weak solution of sulphuric acid and water, slightly heated, will quickly remove discoloration resulting from this cause; or the borax employed as a flux in soldering operations will effect the same result by dissolving the oxide which forms on the surface, while it also protects from further oxidation by excluding the oxygen of the atmosphere. The surfaces to be soldered should be carefully protected from any contact with plaster of Paris, as there is no substance used in the dental laboratory more likely to retard the union of the parts and impair the final result than this.

A solder to be employed in dental mechanics should possess the quality of flowing freely, and be as high in grade as the attainment of that property will permit, so that it will sufficiently resist the action of the fluids of the mouth. It should also approximate as nearly as possible the color of the plate upon which it is used. If the first condition, referring to the contact of the plates to be united, be observed, the quantity of solder required to effect continuity will be reduced to the minimum; and thus we shall have the smallest possible portion of the alloy exposed to the action of the fluids of the mouth, while we at the same time avoid the danger of fracture of the teeth by the contraction in cooling of an inordinate quantity of solder.

The application and management of the heat in the operation of soldering are matters requiring both care and judgment. The temperature should at first be raised very gradually, in order that pieces of solder may not be thrown off or displaced by the puffing-up incident to the calcination of the borax. Both parts to be united should be equally heated; therefore the heat should be so applied in the case of an artificial denture as to raise the teeth and plate to an equal temperature; otherwise, should the plate become sufficiently hot while the teeth remain comparatively cool (a condition likely to occur unless the fuel has been built up around the outside of the investment covering the teeth), the solder, when the flame of the blow-pipe is directed upon it, will flow upon and adhere to the plate. In other words, it will manifest a preference for the hottest portion. The failure to effect an equal distribution of heat preparatory to soldering is often the cause of much vexation and delay. For example, in the process of uniting a rim to a plate by soldering, the rim, being so much smaller than the plate, will be more quickly heated, in which event the solder will fuse and flow upon the rim, and the attempt to unite it to the plate will not be successful. But to avoid such a result, the flame of the blow-pipe should, as a preliminary step, be directed exclusively upon the latter, and union of the rim and plate can hardly fail to take place.

Supports.—In melting small quantities of gold or silver, or in soldering with the blow-pipe flame, it is necessary to perform these operations upon a support made of some suitable body, such as charcoal, coke, pumice-stone, or asbestos and plaster, charcoal and plaster, etc.

Autogenous Soldering.—Autogenous soldering is a sweating process in which a lower fusing alloy is not used. The metallic parts are brought to intimate contact and the pieces heated until the metals fuse upon their surfaces, and thus form a joint. Gold, by using great care, may be soldered in this manner. Lead surfaces are also frequently united by autogenous soldering as in the lead chambers of the sulphuric acid industry.

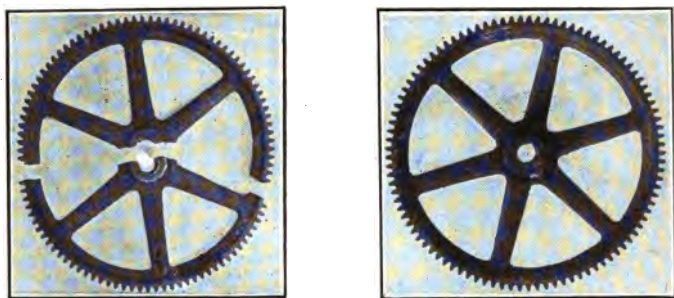


FIG. 42

Welding.—Within the last few years welding, or as it is called autogenous welding, by the use of oxyacetylene gas, has come into use. Extremely high temperatures can be obtained by this mixture of gases, and with the proper form of blow-pipe very neat welding may be accomplished. Another very interesting fact is that a blow-pipe can give a flame that may be used for cutting metals. The author has seen a piece of steel $\frac{1}{8}$ inch thick and 3 feet in breadth cut in a very few minutes by this form of device. Fig. 42 shows a cast-iron gear welded through hub and rim. Large station-

ary machines may be welded without moving them from their positions, which would necessitate a great amount of expense and also in some cases mean the shutting down of the manufacturing plant. The author has seen a weld made of a piece of iron pipe to which was welded an inner tube of copper and then, to this, an aluminum cylinder was welded to the copper.

CHAPTER VI.

COMBINATION OF METALS WITH THE NON-METALLIC ELEMENTS.

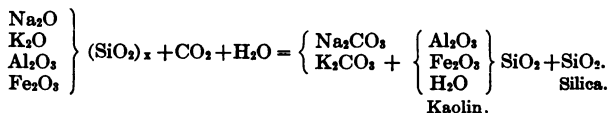
THE metallic elements form chemical compounds with the non-metals. The substances formed in no way resemble the metals entering into their compositions. These compounds are formed in three ways:

(a) By inorganic nature, giving rise to those substances known as minerals.

(b) In the dry way, due to the agency of heat.

(c) In the wet way.

The factors at work in the formation of minerals are: Heat as represented by those substances classified from a geological point of view as belonging to the "igneous period;" water, as in the formation of the so-called sedimentary deposits. At the present time there is a tendency of the natural elements to break down the complex compounds into simpler substances. The breaking up of silicates into carbonates, with the liberation of silicon dioxide, represents this form of phenomenon. The decomposition of feldspar into kaolin and silica is of interest to the dental profession, as all of these materials are used in porcelain bodies. This reaction may be represented as follows:



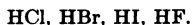
Metamorphic Rocks.—Metamorphic rocks, those formed by an alteration of heat, moisture and pressure, are of especial interest, as the most valuable minerals of the metals are found in metamorphic formations.

Metallic compounds formed in the dry way due to the agency of heat, such as sulphides, silicates, oxides, borates, chlorides, sulphates, are among the compounds commonly met with.

Metallic compounds are formed in the wet way by the action of acids upon a metal; this is one of the most common methods used.

Halogens.—The halogen elements include chlorine, bromine, iodine, and fluorine. Nearly all of the metals combine directly with the halogens. The power of aqua regia¹ to dissolve the noble metals depends upon the liberation of chlorine in the *nascent* state. The compounds of these elements and the metallic elements, may be formed by the following reactions

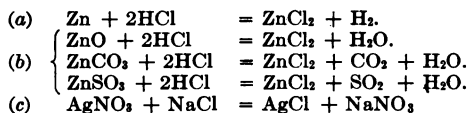
(a) A metal treated with the hydrogen acids of the halogen, *i. e.*:



(b) Oxides, carbonates, and sulphites treated in the same manner as (a).

(c) By double decomposition in solution.

The following reactions illustrate the different methods:

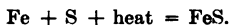


Most of the halogen salts of the metals are soluble in water; the exceptions are lead, silver and mercurous salts. Sodium chloride, silver chloride, silver iodide, silver bromide, cryolite (sodium and aluminum fluoride) are some of the natural occurring compounds of the halogen elements and the metals.

Sulphides.—Sulphides may be formed by heating a metal with sulphur; by passing hydrogen sulphide through a solution containing a metallic salt; by the reduction of compounds containing the metal in combination with sulphur.

¹ Aqua regia, *i. e.*, three volumes hydrochloric with one volume of nitric acid.

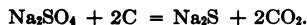
and oxygen (sulphates). To illustrate: iron when heated with sulphur forms iron sulphide—FeS.



Silver combines readily with sulphur; and the tarnishing of silver when exposed to the atmosphere, is due to the formation of the sulphide.

When hydrogen sulphide is passed through a solution of a metallic salt, a sulphide of the metal is formed. The separation of metals in qualitative analysis is based upon the solubility of these sulphides. The sulphides of the alkali and alkali earth metals are soluble in water; iron, cobalt, nickel, manganese and zinc sulphide are soluble in acid solutions, while silver, lead, mercury, copper, cadmium, bismuth, arsenic, antimony, tin, gold and the platinum groups are insoluble in acid or alkaline solution. Chromium or aluminum do not form sulphides in the *wet way*.

Sulphates when heated with carbon, are reduced to sulphides, as the following reaction will show:



The natural occurring sulphides generally have a metallic luster, as in the case of iron pyrites, galena, stibnite, etc. Pyrites has frequently been mistaken for metallic gold and is called "fool's gold." The sulphides are one of the most frequent occurring metallic compounds of the metals and are only exceeded by the oxides.

Oxides.—The oxides of the metals occur in nature, possibly as the result of decomposition of higher compounds of the metals. The noble metals, however, rarely if ever are found as oxides because they are so easily decomposed. Oxides are formed in any of the following ways:

1. By heating a base metal in air or oxygen.
2. By heating carbonates, nitrates and hydroxides.

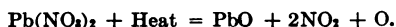
When base metals are heated in air they become oxidized. Sodium and potassium have such an affinity for oxygen that they must be preserved under petroleum.

The kindling temperature of an element is the temperature

at which it unites with oxygen. This temperature varies with the different elements. Magnesium upon oxidation gives off a brilliant white light and is used as a flashlight powder in photography. Aluminum in the finely divided state combines with oxygen giving off so much heat that a temperature of about 3000° C. is reached. The preparation of oxides may be facilitated by the presence of certain substances known as oxidizing agents.

Superficial oxidation may occur by mere exposure to air at ordinary temperatures, particularly in the presence of moisture. It frequently happens, however, that metallic objects thus superficially oxidized are protected by the newly formed oxide from further access of air so that oxidation can no longer go on; but upon the removal of the oxide from the surface oxidation will again occur. When the carbonates are heated, carbon dioxide and water are given off, leaving the oxide of the metal. The preparation of lime from limestone is a practical application of this method of preparation of oxides. Roasting, as has been stated, has for its object the heating of minerals, principally the carbonates, resulting in the formation of oxides.

Nitrates, upon being heated, yield oxides of nitrogen, the oxide of the metal, and in some cases, oxygen.



The hydroxides upon heating form oxides by the driving off of water.



REDUCTION OF METALLIC COMPOUNDS.

The term "reduction," as used in metallurgy, refers to the different methods of separating a metal from its natural ores or from combination with any non-metallic element. In some cases this is effected by heat alone. For example, the noble metals are separated from oxygen by merely heating to 315.5° C. Generally, however, the joint action of

heat and reagents, for which the non-metallic constituents of the compound have greater affinity, is required.

The inventions of Eugene H. and Alfred H. Cowles, of Cleveland, Ohio, and of Graetzel, near Bremen, in Germany, have proved to be a most important advance in metallurgy. The essential features in the improvements made by these gentlemen, is the application of the intense heat of a current of electricity from a dynamo through a conductor of great resistance in the presence of carbon. Many of the most refractory ores, which have hitherto resisted all similar attempts, may be readily decomposed in these electric furnaces. By this means aluminum is now reduced from corundum.¹

The metallic compounds, whether natural or artificial, are a class of bodies formed of dissimilar elements held together by the force of chemical affinity. This affinity varies much in different metals. Thus, gold possesses such feeble affinities that a dilute aqueous solution of gold chloride may be partially precipitated by mere exposure to light. The facility with which gold often passes from one element to another may be observed in the interesting process of manufacturing "shredded gold,"² in which an acid solution of the trichloride is formed and slightly heated in a glass matrass; gum arabic or sugar dissolved in water is then added, when beautiful web-like masses of pure gold are seen to form in the liquid; but unless these are quickly removed by means of a glass spoon or dipper they will almost instantly dissolve and the gold again unite with the chlorine. Lead, tin, zinc, iron, and many other metals evince stronger affinities; hence they are not so readily reduced, and require, in addition to heat, the presence of other substances, such as coal, coke, charcoal, etc. In other words, it is necessary to expose them in contact with some reagent between which, and the non-metallic constituents of the compound, superior affinity exists, so that by union of these the metal

¹ See chapter on Aluminum.

² Lamm's shredded gold."

may be released. It may be said that all analytical operations for the reduction of ores and the detection and estimation of unknown bodies are performed by taking advantage of the different degrees of chemical affinity. Thus, lead which has been overheated or subjected to frequent or long-continued meltings, becomes partially oxidized and covered with an earthy-looking mass consisting of semioxidized metal, formerly called the "calx." Further exposure to heat would simply have the effect of converting this into an oxide of a higher degree; but if covered with finely broken charcoal, or other carbonaceous substance,¹ the latter will extract the oxygen, carbonic dioxide will be formed and evolved, while the metal will be restored to a free state.

Chlorides.—With the exception of the chlorides of the metals of the alkalis and earths, all metallic chlorides are decomposed when heated in a current of hydrogen, hydrochloric acid and the pure metal being the result. The chlorides of gold and platinum are decomposed by simple ignition.

Argentie chlorides when heated on charcoal, under the flame of the blow-pipe, yields pure silver and emits an odor of hydrochloric acid. Placed in water acidulated with sulphuric or hydrochloric acid, argentic chloride may be reduced by the addition of pieces of some easily oxidizable metal, such as zinc or iron, the *rationale* of the reaction being as follows: The zinc displaces the hydrogen of the H_2SO_4 , zinc sulphate is formed, the liberated hydrogen unites with the chlorine to form hydrochloric acid, and pure silver remains.

Concentrated sulphuric acid decomposes the chlorides and converts them into sulphates, the oxygen being supplied from the water present. Some chlorides may be decomposed by heating them with a metal which has more powerful basic properties. Thus, sodium when heated with aluminum or magnesium chloride will become sodium chloride, with

¹ In the dental laboratory beeswax is usually employed to deoxidize lead or zinc which has become thick and earthy by frequent meltings.

liberation of the magnesium or aluminum. Some chlorides are reduced by heating with a mixture of sodic carbonate and charcoal; other carbonaceous compounds, such as sodic or calcium carbonate, are frequently used.

Sulphides.—Reduction of the sulphides in some few instances, such as those of gold, silver, and platinum, is effected by heat alone. The oxygen of the atmosphere unites with the sulphur, which is evolved as sulphur dioxide. In many cases, however, a portion of the oxygen combines with the metal, and an oxide instead of the free metal is obtained. The reduction of many of this class of ores consists simply in such interchanges. The application of heat and air in some instances converts the sulphide into a sulphate which in turn may be decomposed at high temperatures and separated into sulphur dioxide and a metallic oxide. On the other hand, some of the sulphides may, when heated with access of air, be converted into permanent sulphates capable of resisting high degrees of heat. The sulphides of the noble metals, when heated, part directly with the whole of their sulphur, leaving the metal in a pure state. Silver sulphide thus reduced is also partially oxidized, so that a small portion of argentic sulphate is formed, which requires for its reduction a still greater elevation of temperature.

Agents, such as metallic iron, hydrogen, chlorine, etc., are frequently employed to combine with sulphur. If sulphide of lead be heated with iron, sulphide of iron and metallic lead result. This method is practised in the assay of galena, clean iron nails being heated with the ore. The sulphides of antimony, bismuth, copper, tin and silver are readily reduced by passing dry hydrogen over them at red heat, the result of the reaction being the free metal and hydrogen sulphide. Dry chlorine will also decompose them and combine with both the metal and the sulphur. Nitrohydrochloric acid converts the sulphides into chlorides, and hydrochloric acid in a few instances acts similarly; its hydrogen, combining with sulphur, is evolved as hydrogen sulphide. Strong nitric acid decomposes them, and is often employed in analyses of ores. The sulphur being thus oxidized, the liberated

metal combines with the acid to form a nitrate, mercuric sulphide or native cinnabar being the only ore which cannot be thus reduced.

Oxides.—The reduction of lead, zinc, or tin, the working qualities of which have been impaired by frequent meltings with exposure to air, may be affected in the laboratory by placing the metal to be treated either in a large clay crucible or in the ordinary iron melting pot employed by dentists. The semioxidized metal is then covered with powdered charcoal, when the reaction described above takes place, and the original properties of the metal are restored. There are some oxides to which the foregoing treatment is not applicable, but these may be reduced by passing a current of dry hydrogen over them when heated to redness. Makins gives the following very clear description of this method of reducing oxides:

“A large two-necked bottle is fitted up in the usual way for the evolution of hydrogen. This has its delivery tube passed into a tube filled with fragments of calcium chloride, for the purpose of absorbing the moisture which may be carried over with the gas; to the other end of this drying tube is connected the tube which is to hold the metallic oxide (generally in a bulb blown upon this). The gas bottle should contain about a couple of quarts, so as to afford a steady supply; the calcic chloride tube should be long and well filled. In operating, after the gas has completely driven out the air in the apparatus, heat is applied to the bulb containing the oxide, and its reduction will be brought about. The gas must be kept up in a good stream, so as to drive out the watery vapor formed by the decomposition. Here the hydrogen takes the oxygen of the oxide, and water is formed, while the metal is set free.”

There are metals whose affinity for oxygen is so strong that their union with that element cannot be broken by such means as we have described. Deoxidation of these metals must be performed through the agency of some other metal possessing greater affinity for oxygen. For example, if oxide of iron be heated with potassium the iron will be

deoxidized, while the potassium will be converted into (K_2O) potassium oxide.

Some metallic oxides may be reduced by heating with sulphur, part of the latter abstracting the oxygen, with which it unites to form sulphurous acid. A portion of the sulphur, however, unites with the metal, which is converted into a sulphide, or a sulphate, or a mixture of both. These must then be treated according to the directions already given for the reduction of metals when combined with sulphur.

There are also a few metallic oxides which chlorine gas will reduce. Thus, platinum is liberated from combination with oxygen when exposed to a current of dry chlorine.

Probably the most powerful means of reducing metals from combination with non-metallic elements is that known as electrolysis. It consists in exposing a solution of a metallic salt to the decomposing influence of the galvanic current. A demonstration of this force may be made by taking a solution of lead nitrate and immersing in it a piece of zinc. The latter soon becomes covered with needle-like crystals of pure lead; the zinc replaces the lead, which is set free and decomposed at the point of galvanic action. Or, the same phenomenon may be witnessed by immersing a piece of clean iron in a solution of copper or a piece of copper in a solution of a salt of mercury,¹ the action only ceasing when all the metal in the solution is reduced.

¹ Reinsch's test for the detection of the mineral poisons is based on this principle.

CHAPTER VII.

LEAD.

Symbol, Pb (plumbum). Atomic weight, 206.9.

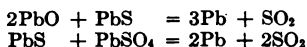
Occurrence.—In the free state it occurs in small quantities associated sometimes with a little antimony or silver. In combination as galenite or galena, PbS , usually with some silver, and frequently sulphides of antimony, bismuth and cadmium. Cerussite, PbCO_3 , the native carbonate is also a very important ore of lead. Among the less important ores of lead may be mentioned anglesite, PbSO_4 ; pyromorphite, $\text{Pb}_5\text{Cl}(\text{PO}_4)_3$; wulfenite, PbMoO_4 .

Historical.—Lead has been known from very remote times, although the material termed lead as used today differs from that mentioned in the very early writings of the Bible. The ores of lead are so comparatively easy to reduce, one may see how the ancients with their crude methods could very easily reduce this material. The metallurgical importance of lead may very easily be conceived when we stop to consider that the world uses nearly 900,000 tons of lead per year; this country produces nearly one-third of this amount. About one-half of the output from the United States was desilverized. Among the principal uses of lead may be enumerated the following: (a) Manufacture of white lead; (b) preparation of oxides of lead; (c) shot, lead pipe and sheet lead; (d) preparation of alloys.

Reduction.—Three methods of smelting are available:

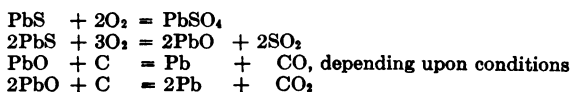
1. *Air-reduction Process.*—The galena is first roasted to such a degree that a mixture of lead sulphide, oxide and sulphate is produced, and then the temperature is raised and the oxide and sulphate react with the remaining sulphide producing metallic lead and sulphur dioxide.

Reactions:

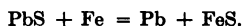


2. *Roasting and Carbon-reduction Process.*—Roasting the galena until it is entirely decomposed or is practically converted into lead oxide mixed with a small amount of sulphate; this is then reduced with carbon. Special procedures are used to recover the lead from the sulphate.

Reaction:



3. *Precipitation or Iron-reduction Process.*—Galena is decomposed by heating with metallic iron, lead being set free and sulphide of iron and lead (lead matte) is produced.



The process used is dependent upon conditions. The iron reduction process seems to be the simplest procedure, but this reaction is only carried on at a high temperature which would demand the presence of cheap fuel in the locality in which the reduction was carried on, also the presence of lead in the matte must be recovered by a subsequent treatment; both of these factors must be taken into consideration. From an economical point of view it has been found that the best practice is to make use of two or all of the above processes in the commercial reduction.

The lead first obtained by any of these processes usually contains copper, antimony, tin, and other metals. These are removed by heating the metal in a shallow, flat-bottomed reverberatory furnace. Most of these metals oxidize before the lead, and collect in the dross which forms on the surface. This process is known as the softening of lead. The silver, which is always present is not removed by this process, but is extracted by one of the special methods for desilverizing lead described under Silver.

The wet processes are not used for the reduction of lead, but the electrolytic method has been tried in several localities. The lead is obtained from this process as a spongy mass. For the most part this method has not proved a financial success.

Properties.—Lead is a bluish-white metal, with a distinct metallic luster when freshly cut; it loses its luster upon exposure to air due to the formation of the suboxide. Lead is sufficiently soft to be scratched with the finger-nail, ranking about 2 in the scale of hardness; it leaves a black streak when drawn across paper, and is generally considered the softest of the ordinary metals; the presence of other metals makes lead sensibly harder. It is a very poor conductor of heat and electricity. Lead ranks low in tenacity, for this reason it cannot be drawn into a very fine wire although it may be rolled into sheets, and this form of lead was used at one time as a filling material in dentistry. When lead is fused and the temperature raised its surface assumes first a yellow and then a cherry hue and appears crystalline upon cooling; when partially solidified octohedral crystals belonging to the regular system are obtained. It melts at 326° C., 618° F., boils white heat, vaporization begins at 360° . Its specific gravity is 11.38. Specific heat 0.0314. Coefficient of linear expansion between 0° and 100° C., 0.000028575. Coefficient of thermal conductivity in C. G. S. units is 0.081. As a conductor of electricity, 20.38.

It has no taste but possesses a peculiar odor when freshly cut. Lead alloys with most metals with the possible exception of zinc, in the latter case it seems as if these two metals are without affinity and are only very slightly soluble in each other. Lead is a very important metal in the cupellation process in the separation of gold and silver from their ores.

Lead possesses the property of solid flow to a remarkable extent; advantage is taken of this fact in the manufacture of lead pipe, and it may be also pressed into wire of a much smaller gauge than could be obtained by the use of the draw-plate.

In the manufacture of shot a small percentage of arsenic is

added to the lead, this increases its hardness and also makes the lead flow more readily and assume the spherical form.

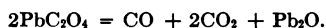
From lead solutions, Zn, Mg, Al, Co and Cd, precipitate metallic lead.

Solubilities.—Lead dissolves very readily in nitric acid, but sulphuric and hydrochloric acids are almost without action upon it in the cold. Hot concentrated hydrochloric acid slowly converts it into lead chloride. Sulphuric acid of a specific gravity higher than 1.6 attacks lead and the lead sulphate formed is soluble in the concentrated acid; this accounts for the presence of lead sulphate as an impurity in commercial sulphuric acid.

Lead is soluble in pure water in the presence of air, forming the hydroxide; this compound is slightly soluble in water and may be a source of lead poisoning. As most of the potable waters contain carbon dioxide in solution, the lead hydroxide is precipitated from the water as the basic carbonate.

Oxides.—Lead forms four oxides, Pb_2O , PbO , Pb_3O_4 , PbO_2 ; a fifth oxide is sometimes mentioned, Pb_2O_3 .

Lead Suboxide (Plumbous Oxide), Pb_2O .—Lead suboxide is a black oxide formed when lead is heated to its melting point. It may also be obtained by heating lead oxalate, PbC_2O_4 , to 300° in a glass tube excluding air.



When the suboxide is heated in air it burns, forming plumbic oxide.



Plumbic Oxide (Lead Monoxide, Litharge, Massicot), PbO .—Plumbic oxide is formed when lead is strongly heated in air and may be obtained by heating the nitrate or the carbonate. It is a yellowish powder and when heated melts and may be obtained in crystal form. Lead monoxide is soluble in acids and also in warm sodium or potassium hydroxide. With acetic acid in the presence of an excess of oxide it forms basic lead acetate which is used in medicine under the name "Goulard's Extract."

Lead Sesquioxide, Pb_2O_3 .—Lead sesquioxide is described as an orange-colored precipitate formed when sodium hypochlorite is added to a solution of plumbic oxide in potassium hydroxide. This compound is generally considered a mixture of PbO and PbO_2 .

Triplumbic Tetroxide (Red Lead, Minium), Pb_3O_4 .—Triplumbic tetroxide, obtained by heating PbO for some time at a temperature slightly above 450° . At a higher temperature it gives up its oxygen and is again converted into PbO .

Plumbic Peroxide (Lead Dioxide), PbO_2 .—Plumbic peroxide is obtained by fusing PbO with potassium nitrate or potassium chlorate. It is a brown-colored powder and a very powerful oxidizing agent.

Dental Uses.—Lead is used in the construction of counter-dies. The prosthesis in constructing metallic bases generally obtains a counter-die of this metal by pouring the molten lead upon the die, which is constructed of some higher fusing metal or alloy. In crown and bridge-work a counter-die may be made in a similar manner or by simply hammering the die into a piece of lead. Lead being a very soft metal will not destroy the fine lines of the die in the latter process. Lead points have been used as a root canal filling material. It is also a constituent of the various low fusing alloys (see bismuth). In filing lead or alloys containing large proportions of this metal coarse files should be used, as it is prone to cling to the rasps of the file and is very difficult to remove, thus ruining the file. In the form of shot, lead is also used in the process of swaging metals to a die, the shot being placed in some form of a retainer. This method is used when the die is constructed of a metal or alloy of a low fusing point, in which there is a liability of the molten lead injuring the die.

Lead and mercury readily amalgamate; this may be accomplished by treating lead filings with mercury or by fusing the lead and mercury, then adding mercury. Lead amalgam is crystalline in structure and very brittle.

As prepared by the first process the amalgam sets very slowly. I have specimens of this amalgam which were prepared seven years ago, and have been kept in tightly

corked bottle. The mass is almost devoid of cohesive properties, shows evidence of decomposition and when placed between the fingers emits a cringing sound showing it to be crystalline in nature. When prepared by the second method the amalgam has a metallic luster, may be readily carved with a penknife and a specimen one-half inch in thickness may be readily broken between the fingers. Upon standing it loses its metallic luster and resembles lead in color. This amalgam has no properties which would recommend it to be used in dentistry. Lead and gold are miscible in all proportions and form two compounds, AuPb_2 melting at 300°C . There is also a eutectic which melts at 215°C ., corresponding to the formula AuPb_2 . These alloys are all very brittle and because of their comparatively low fusing point great care should be taken not to contaminate gold with lead. In swaging gold on a lead counter-die the surface of the gold should be protected from coming in actual contact with the lead, as there is a possibility of contamination. If the gold is placed in hydrochloric acid as a pickling solution the lead would not be removed, as lead is insoluble in this acid. Gold containing extremely small quantities of lead cannot be used for coinage.

Silver and lead mix in all proportions. It forms a eutectic consisting of 98 per cent. Pb and 2 per cent. Ag., melting at 305°C . It does not form chemical compound or mixed crystals. By taking advantage of this eutectic, silver may be recovered from lead as is described under Desilverization of Lead.

Lead and platinum are said to form a peculiar alloy which has a low fusing point and very brittle. These two metals cannot be separated by cupellation, as the lead oxidizes; an alloy rich in platinum is formed which has a fusing point higher than the temperature of the muffle.

Palladium forms a brittle alloy with lead. Tin and lead unite in any proportions, and these alloys are used as soft solders. Dr. Haskell's counter-die metal consists of 1 part tin and 5 parts lead.

Antimony is alloyed with lead to increase its hardness.

RESUMÉ.

Symbol, Pb.	* Specific gravity, 11.38.
Valency, II and IV.	Crystalline form, octohedral.
Atomic weight, 206.9.	Chief ore; galena.
Melting point, 326.9° C.	Conductivity of electricity, 20.38.
Specific heat, 0.0314.	Conductivity of heat, 85.
Boiling point, 327° C.	Coefficient of expansion,
Malleability, 7th.	0.000029.
Ductility, 8th.	Tenacity, 8th.

CHAPTER VIII.

MERCURY.

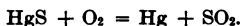
Symbol, Hg (hydrargyrum). Atomic weight, 200.6.

Occurrence.—Mercury occurs in nature in the native state sometimes containing a little tin, gold or silver. The sulphide, cinnabar HgS , is the principal ore. The ore is usually low grade and that found in this country yields on an average, less than 1 per cent. mercury. There is also a chloride, Hg_2Cl_2 , horn mercury, but this is found only in small quantities. The chief mines are those of Almaden in Spain, Idria in Austria, California and the Bavarian Palatinate.

Historical.—Mercury has been known from remote times and was considered as the type of the metallic character. One of the first endeavors of the alchemist, in his efforts to change base metals into gold or silver, was the fixing of the mercury, thus making the base metal non-volatile. In the fifteenth century the powerful medicinal properties of mercury were discovered; this fact together with the views held by the alchemists caused the study of mercury to be advanced at a very early period.

Reduction.—There are three processes of reducing mercury from the sulphide ore; the first process is the one most commonly used at the present time.

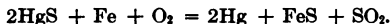
1. The sulphide ore is washed, whereby the sulphur is oxidized to sulphur dioxide and the metal liberated from combination.



2. The sulphide is heated, in a closed retort with lime; calcium sulphide and sulphate are formed and the mercury set free. Reaction:



3. Cinnabar is heated with iron and the following reaction takes place:



In the first process the sulphide is heated in kilns where the reduction takes place. The temperature of the kilns is sufficiently high to volatilize the reduced mercury, the vapor of which passes into brick condensing chambers (Fig. 43, C). For dental purposes the mercury is again distilled to remove the least trace of base metal with which it may be contaminated. This product is known as redistilled mercury.

Commercial mercury may also be purified by the electrolytic process. By this method it may be freed from admixtures of zinc, cadmium, bismuth, lead and tin. A crude test which is often used to discover if mercury contains base metal impurities is to allow some of the mercury to flow over a piece of white cardboard. If the mercury leaves a track or

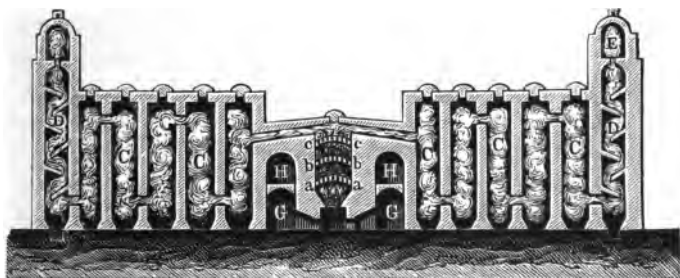


FIG. 43

tail, base metals are present; however, mercury which will not show this reaction may still contain impurities in sufficient amounts to render it useless for dental purposes.

Properties.—Solid mercury exists only at a temperature below -39.44°C. , and at ordinary temperatures it is a liquid, being an exception to the general statement that metals are solids at ordinary temperatures. The solid metal is very ductile and is so soft that it may be cut with a knife. It ranks low in heat and electrical conducting powers, and also has a low coefficient of expansion on heating. During solidification it contracts considerably, its specific gravity rising from 13.59 to 14.19 and forms octahedral crystals. Mercury in extremely thin films appears a violet color by transmitted light.

Under a pressure of 760 mm. mercury boils at 357.25° ,

giving a colorless vapor. Mercury does not tarnish upon exposure to the air and is classed as a noble metal. Mercury is obtained in the form of a dull gray powder when it is shaken up with oil or triturated with sugar, chalk, or lard. This operation is known as deadening, and is made use of in the preparation of mercurial ointments. The gray powder consists simply of very finely divided mercury in the form of minute globules. Most of the soluble salts and also the vapor of mercury is poisonous, and when an alloy containing mercury is heated to a temperature at which the mercury is volatilized care should be taken not to inhale the fumes; it is best to place the materials in a *hood* while heating.

Solubilities.—Mercury is not attacked by alkalis. The most efficient solvent is nitric acid. It dissolves readily in the dilute acid hot or cold; with the strong acid, heat is generated, and with considerable quantities of material the action acquires explosive violence. Concentrated sulphuric acid at ordinary temperatures does not attack mercury, but with the hot acid sulphur dioxide and mercuric sulphate are formed. Hydrochloric acid even in the concentrated form has very little action on mercury; chlorine, bromine, and iodine, dry or moist attack the metal. Hydrobromic and hydroiodic acids attack mercury-forming mercurous bromides and iodide with the evolution of hydrogen.

Compounds.—Mercury forms two oxides: Mercuric oxide, HgO , is a brick-red crystalline powder when prepared by prolonged heating of the metal, heating the nitrate or by heating a mixture of mercuric nitrate and mercury. Mercurous oxide is an unstable brown or black powder and may be prepared by adding sodium hydroxide to mercuric chloride solution. This compound when gently heated changes to mercuric oxide. Mercury forms two chlorides: Mercurous chloride, Hg_2Cl_2 , known as calomel, is insoluble; mercuric, HgCl_2 , corrosive sublimate which is soluble. Mercuric chloride is a very valuable salt because of its antiseptic properties and is extensively used in medicine.

Vermilion.—With sulphur, however, mercury combines to form sulphates and sulphides. Of the latter we have mercuric sulphide (HgS), a compound of great interest to

dentists in consequence of its extensive use as a coloring pigment in vulcanizable rubbers and celluloid. It is the most common ore of mercury, and, as such, is termed cinnabar; when produced artificially it is known as vermilion. The best quality of the latter is made by the Chinese. Their process of manufacturing, for a long time a secret, consists in stirring a mixture of one part sulphur and seven parts of mercury in an iron pot; chemical union takes place, the result of the combination being a black powder. This is divided into small lots, which are emptied separately into suitable subliming pots, heated to redness. When a sufficient quantity has been placed in the pots they are covered up, and the heat is continued for thirty-six hours, with occasional stirring by means of an iron rod passed through the lid. Lastly, the pots are broken and the vermilion adhering to the upper portions levigated and dried. It may also be formed by rubbing 300 parts of mercury with 114 parts of flowers of sulphur, moistened with a solution of caustic potash. The resulting product, which is black, is then digested at about 49° C., with 75 parts of caustic potash and 400 parts of water, until it acquires a fine red color.

Vermilion may be adulterated with red lead, sulphide of arsenic (As_2S_3), ferric oxide, brick dust, or any cheaper substance of a similar color; and the discomfort sometimes caused by wearing vulcanized rubber artificial dentures may be in part due to the presence of such deleterious substances as the arsenic and lead salts referred to.

Tests for Vermilion.—In order to see at once whether a given red paint is cinnabar, minium (Pb_3O_4) or ferric oxide, moisten the object with ammoniacal solution of AgNO_3 . It will turn black at once if it is HgS , due to the formation of Ag_2S and $\text{HgNO}_3 \cdot 3\text{NH}_3$. In order to see if a given sample is all HgS or a mixture, heat some of it in a porcelain crucible to a red heat. *If it evaporates*, the paint is pure HgS .

Vermilion is an inert mercurial compound, and both the black and the red varieties are quite insoluble in acids; only concentrated HNO_3 and aqua regia decompose it. It is unaffected by water, alcohol, or the alkalis. It is soluble in concentrated solution of K_2S , Na_2S , $(\text{NH}_4)_2\text{S}$, when these

sulphides contain KOH, NaOH or NH_4OH . From the solutions colorless crystals of HgS , $2\text{K}_2\text{S}$, $\text{Hg}_2\text{Na}_2\text{S}$ deposit, but water decomposes these double sulphides at once. It is also soluble in cold concentrated hydriodic acid and in warm dilute hydriodic acid.

Pure vermilion, in combination with rubber, is not likely to produce deleterious effects when worn in the mouth, nor is it probable that this compound can be decomposed chemically and converted into a poisonous salt of mercury by mere contact with the saliva. The mechanical dentist will, however, do well to avoid the use of nitrohydrochloric acid in removing tinfoil from the surface.

Regarding the presence of free mercury in rubbers before or after vulcanizing, Prof. Austen stated that the researches of Prof. Johnston with the microscope, and of Prof. Mayr by chemical analysis, failed to discover the slightest trace in samples of that which had been used by him for several years. Prof. Wildman observed that sulphur sublimed during vulcanization, but did not find the smallest trace of free mercury. Prof. Austen failed by mechanical force to press out any metallic globules, and during his entire experience with indurated rubber as a base for artificial dentures never, even with the microscope, detected the slightest particle of metallic mercury upon the surface of any finished piece.

If it is true, as some assert, that free mercury has occasionally been observed in rubber, then its presence must have been due to the use of an imperfect quality of vermilion; but that the latter, when pure, is ever reduced during the process of vulcanizing, or by wearing in the mouth, is not at all probable.

Amalgams or Mercury Alloys.—Mercury is miscible with most metals, in some cases chemical compounds are found and in others mixed crystals. (The amalgams will receive due consideration in Chapter XXIV.)

Tin Amalgam.—Ordinary mirrors are made by covering one side of a polished glass plate with sheets of tinfoil, Upon the latter, mercury is rubbed by means of a soft brush; thus a crystalline film of tin amalgam forms on the glass.

The alkali metals combine with mercury with a great rise of temperature. In contact with water these amalgams decom-

pose; hydrogen being evolved, and the alkaline hydroxide formed. On this account sodium amalgam is frequently used in the laboratory as a reducing agent. Upon heating to 440° these amalgams leave behind crystalline compounds, K_2Hg and Na_3Hg , which spontaneously inflame in contact with air.

The alkali amalgams are also used in the amalgamation process in the extraction of silver and gold from their ores.

Zinc amalgams are only very slowly acted upon by dilute sulphuric acid; therefore by the superficial amalgamation of the zinc plates used for galvanic batteries, the same result is obtained as though the zinc were perfectly pure, and no solution of zinc takes place until the electric circuit is closed.

Ammonium Amalgam.—When an amalgam of sodium and mercury is thrown into a solution of ammonium chloride, ammonium amalgam is formed. This amalgam may also be formed by passing an electric current through a solution of ammonium chloride or other ammonium salt, the solution standing over mercury which forms the cathode, the mercury begins to swell up to form five to ten times its original volume in absorbing 0.1 per cent. of its weight of ammonium. The sponge-like amalgam formed in the first process is generally believed to consist simply of mercury inflated by hydrogen and ammonia gas. When the mass is subjected to pressure it obeys Boyle's law, that is, its volume is in inverse proportion to the pressure. Upon standing this amalgam breaks up, liberating mercury, hydrogen, and ammonia; however, one-half of the hydrogen is occluded with the mercury.

RESUMÉ.

Symbol, Hg.	Crystalline form (solid), isometric.
Valency, I or II.	Chief ore, sulphide, cinnabar.
Atomic weight, 200.6.	Conductivity of electricity, 1.69.
Melting point, -39.44° C.	Conductivity of heat, 13.
Specific heat, 0.0332.	Coefficient of expansion, 0.000181.
Color, white.	
Boiling point, 357° C.	
Specific gravity, 13.59.	

CHAPTER IX.

SILVER.

Symbol, Ag (argentum). Atomic weight, 107.88.

Occurrence.—Native silver is found in nature but not to the extent to which native gold occurs. Native silver may contain the following metals as impurities: gold, copper, platinum, mercury, bismuth and antimony. The native amalgam, Ag_2Hg_3 to Ag_{36}Hg is found crystallized as isometric crystals.

In combination silver occurs as: the sulphide, argentite, cerargyrite, horn silver, AgCl ; also as the sulpho-arsenite and sulpho-antimonite. It is also found as impurities in other ores, as: manganese, lead and copper. Ordinary silver ore contains less than 1 per cent. of the silver compounds distributed through various earthy minerals and shows the true nature of the silver-bearing substance in occasional rich specimens. Silver and its ores are found in the following localities: Norway, Peru, Northern Mexico, Michigan, Colorado, Montana, Idaho and Arizona, in the native condition; in combination, various parts of the United States, South America and Europe.

Historical.—Silver is one of the longest known metals, possibly because of the fact that it occurs in the native metallic condition.

Reduction.—The method of extracting silver may be classified into three groups:

1. Dry processes.
2. Wet processes.
3. Electrolytic processes.

To a certain extent the wet and dry methods of extraction are combined, argentiferous products obtained by dry methods

being worked up by wet methods, or *vice versa*. Electrolytic processes are usually preceded by a preparation of the ore by dry methods.

The extraction of silver from ores and smelting products in the dry is based upon the conversion of the silver into a silver-lead alloy, while the combined wet and dry methods include:

- I. The conversion of silver into silver-lead alloy.
- II. The production of silver amalgam.
- III. The production of silver compound which is soluble in aqueous solution.

Amalgamation Process.—The silver is first converted into the chloride by roasting with salt, the silver chloride formed is then reduced by metallic iron or copper and the reduced silver amalgamated.

The chloridizing roasting of the ore is carried out in reverberatory furnaces and the reduction of the chloride and amalgamation of silver is effected in some form of amalgamating apparatus.

The ore is first dried and then submitted to dry stamping; in some localities the sodium chloride for the next step in the reduction is also dried, the object of this procedure is to prevent the formation of sulphuric acid during the chloridizing.

In the next step in the chloridizing roasting of the ores it is necessary that manganese dioxide be present in small quantities; if this is not present a certain amount of pyrites is added to decompose the salt. The chloridizing roasting is also an oxidizing roasting, the sulphides present being converted into oxides and sulphates. The free chlorine converts compounds of metallic sulphides with arsenic and antimony sulphides into metallic chlorides with the production of chlorides of sulphur, arsenic and antimony. The products of the roasting operation contains the greater part of the silver as chloride, together with some unaltered silver ore, also other metallic impurities. At the present time it is not customary to continue the roasting until all of the silver has been converted into the chloride, but the furnace is allowed

to cool slowly and a further chloridizing takes place. The result is that 95 per cent. of the silver may be converted into the chloride.

Barrel Amalgamation.—The roasted ores still containing an excess of salt are first treated for some time with water and pieces of iron in rotating barrels. The salt dissolves in the water and the brine dissolves silver chloride, the iron reducing this to metallic silver. The barrels are agitated for a few hours and mercury is then added. The silver set free by the iron is then taken up by the mercury, forming an amalgam. The water is then drawn off and the amalgam is run off in troughs and collected. The amalgam is then pressed in canvas bags to separate the excess mercury. If the canvas bags are simply drained the mercury will contain only 0.06 per cent. of silver, while if the bags are pressed 1.12 per cent. of silver is lost. The silver amalgam is then retorted in cast-iron tubes.

The Patera Process.—This process is used in Central America and Mexico where fuel is scarce. The essential features of this process are: the ore is finely pulverized and the moistened ore is made into heaps after being intimately mixed with sodium chloride, copper sulphate and mercury. The mixture is then placed on floors impervious to mercury, generally made of asphalt or cement, it is allowed to partially dry, then mules or horses are driven over the mass and in this way trituration is obtained. The amalgam is collected by placing the ore in vats containing water. The collected amalgam is filtered through cloth bags and the mercury from the amalgam volatilized by heat.

Dry Methods.—The extraction of silver from its ores in the dry way is effected by converting the metal into a silver-lead alloy and then submitting this to an oxidizing melting in the cupellation furnace. Lead possesses the property of readily alloying with silver and extracting the silver from various other compounds present in the ore; the operation is carried out either by simply melting or by a combination of roasting and melting processes. If the amount of silver in the lead is not sufficiently great to render direct cupellation

profitable, then it is concentrated before being cupelled. This concentration of the silver in the lead is effected by two processes, Pattinson's process and Parker's process.

Pattinson's Process.—This process was described by Pattinson in 1833. He observed that if molten argentiferous lead be slowly cooled, the portions solidifying first are crystalline and much poorer in silver than the still liquid portions. If the liquid portion be separated, it can again be separated into a poorer solid portion and still richer alloy, this separation can be continued until the lead contains 2.5 per cent. silver. After this point is reached no further separation is possible and the liquid portion will have almost the same silver content.

In the hand process, this process is carried out in hemispherical pots of cast-iron. They are usually 5 feet in diameter, 35 inches deep, $1\frac{1}{2}$ inches thick at the bottom, and 1 inch thick at the top; each pot holds about 10 tons of lead. The lead is melted in the pot and any scum or dross forming on the surface is skimmed off and, if necessary, a further purification by poling is resorted to. When the lead is freed from impurities the fire in the grate is withdrawn or generally transferred to the grate of the adjoining pot, and the surface of the molten metal is carefully sprinkled with water. In consequence of the slow cooling which ensues, crusts form upon the surface and sides of the bath of metal, and these are thrust down and mixed up with the rest of the metal in order to insure a uniform reduction of temperature. As soon as the surface of the bath becomes uneven and the metal is of an almost semipastry consistency, crystallization is sufficiently advanced and the work of ladling out the crystals begins. This is effected by two or more workmen, working at one or on two opposite sides of the pot with perforated ladles, and either $\frac{2}{3}$ or $\frac{3}{4}$ of the contents of the pot is removed as crystals, according to whether the thirds or eighths system of working is in use. The volume of the crystals ladled out is measured by means of a right-angled measure laid across the top of the pot.

The enriched third or eight of the original lead is either

ladled out of the pot into an adjoining one in the system of thirds or else cast into molds. The crystals obtained in this way are small elongated octohedra united along an edge, which, as they only grow in one direction appear as long, four-sided pyramids.

To the crystals which have been ladled over, a quantity of lead of the same silver content is now added, so that the pot again contains its normal quantity; that is, with the thirds system $\frac{1}{3}$ of the normal contents of the pot. To the mother liquor remaining behind, $\frac{2}{3}$ of the volume of the pot of lead of the same silver content as the mother liquor must be added. Then in most cases the operation of the desilverization is repeated just as the case of the pot full of the original lead. In the thirds system, the entire quantity of argentiferous lead is in the pots, of which there may be 15 in number.

In the system of eighths, from 2 to 6 pots are worked together but the process does not go on uninterruptedly as in the thirds system until lead of the requisite content is produced. The following is a description of the thirds system (Freiburg) in which 14 pots are used. The lead containing 0.02 per cent. of silver is changed in the pot No. 7 and after it is melted and cooled, $\frac{2}{3}$ of its contents in crystal form are ladled to pot 8, the remaining liquid $\frac{1}{3}$ being put into pot No. 6; in order that fresh crystallization can be effected in pots 6 and 8, they have added to them $\frac{2}{3}$ and $\frac{1}{3}$ respectively of the contents of lead of the same percentage of silver as each of them contain, from stock reserves. The contents of both of these pots are now melted and allowed to crystallize, and then $\frac{2}{3}$ of the contents of pot No. 6 crystals are ladled out into pot No. 7 and the remaining $\frac{1}{3}$ of the molten liquid is put into pot No. 5; from the eighth pot the crystals are ladled to pot No. 9 and the mother liquid go to pot No. 7. Pot No. 7 has in this way received another full charge, while pots Nos. 5 and 9 are made up of the requisite quantity by the addition $\frac{2}{3}$ and $\frac{1}{3}$ respectively.

Pots 5, 7, and 9 are crystallized and after them 4, 6, 8, and 10; and by continuing the working in this way, poor lead is at last obtained with 0.002 per cent. of silver and rich

lead with at least 1.5 per cent. of silver. The silver from the rich lead may be recovered either by cupellation or submitted to the zinc desilverizing process.

Zinc Desilverizing Method (Parker's Process).—If 1.5 to 2 per cent. by weight of zinc is added to argentiferous lead in the molten condition and thoroughly stirred, then allowed to cool, a crust or scum forms upon the surface as the tem-

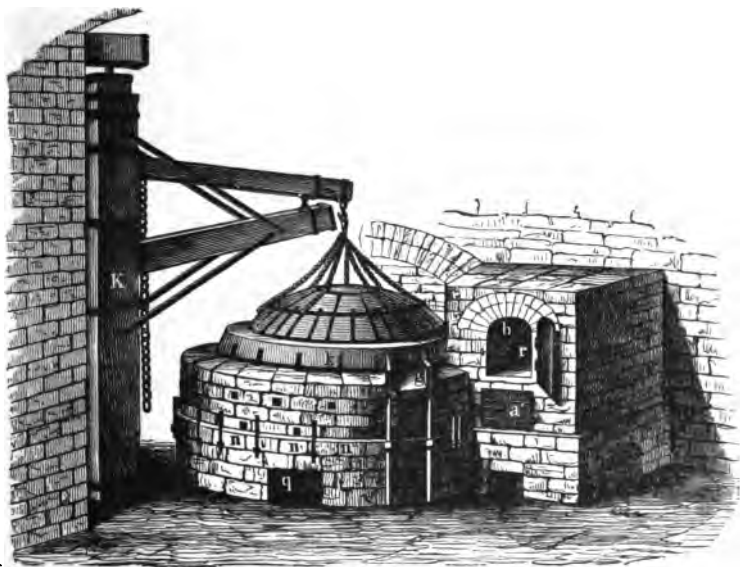


FIG. 44

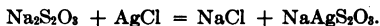
perature is allowed to fall. This scum is a solidified mixture of alloys of lead, zinc and silver, lighter than the molten lead and containing all the silver originally present in the lead, and can be easily separated from the rest of the metal. The zinc and lead can then be driven off from the silver by distillation and cupellation.

The cupel (Fig. 44) is made of a fire-clay mixture, in the hearth of a reverberatory furnace; *r* represents the muffle

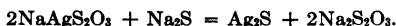
which has a concavity oval in shape. The rich lead is placed in the muffle and brought to redness, and air is blown over the surface. Lead changes to lead oxide, which runs off until finally only silver, with some 5 per cent. of lead, remains. This is refined in a new hearth and with higher heat.

Wet Process (Ziervogel Process).—When argentiferous pyrites, or an artificially formed regulus containing sulphides of silver, copper and iron is roasted, the sulphides are first converted into sulphates and, as the roasting continues, first the iron, tin, copper and lastly the silver sulphate is converted into oxide. By carefully watching the process all of the iron and part of the copper sulphates are decomposed. On lixiviating the roasted mass with water, the silver sulphate together with the remainder of the copper sulphate dissolves. From this solution the silver is precipitated by scrap copper.

The Percy-Patera Process.—The ore is roasted with salt and the silver chloride so formed is then extracted by means of sodium thiosulphate



To this solution so obtained sodium or calcium sulphide is added which precipitates silver sulphide



The silver sulphide is then reduced by roasting in a reverberatory furnace.

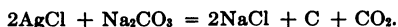
The electrolytic process requires the conversion of the silver into a copper-silver, lead-silver, zinc-silver or gold-silver alloy and the silver collects at the anode (positive pole) in all cases except when gold-silver alloy is used, and then it collects at the cathode (negative pole). The silver which is deposited contains various impurities which must be removed by special processes. Preparation of chemically pure silver.

Pure Silver.—Pure silver, which is reckoned as 1000 fine, may be obtained from standard or other grades of silver by dissolving the granulated metal or copper alloy in HNO_3 , sp. gr. 1.20 (conc. HNO_3 with an equal volume of distilled

water). Heat facilitates the solution of silver in the HNO_3 . Dilute the solution with 20 volumes of distilled water. Add HCl so long as precipitate keeps forming, stir vigorously and let settle. Drain off the liquid and wash with cold water until filtrate shows no trace of copper. Boil the silver chloride with aqua regia (1 to 3) for a greater or less time, according to quantity, one hour for 100 grams, two hours for 500 grams. Drain again and wash with distilled water, until all acidity has been removed. Now add 10 per cent. solution KOH so that the KOH in it equals the weight of silver chloride; add an equal amount of pure glucose and boil until chloride has become a dark gray, fine metallic powder; drain and wash thoroughly until all alkali reaction disappears. Dry the powder at about 150°C . It is pure silver, and is kept best in this shape for use in the laboratory. You may melt it, or some of it, in a cavity on a purified piece of charcoal, or in a crucible which has been lined with pure charcoal powder. In the first case use the Bunsen gas blow-pipe, in the second a gas or wind furnace. Pouring the molten metal from a height of several feet into water will convert it into granules. In hammering or rolling silver it must be heated to redness at regular intervals, as the mechanical shocks cause a certain brittleness, the metal tears at the edges.

Another method of precipitating silver in the metallic form consists in placing a sheet of copper in a solution of argentic nitrate. The metal is thrown down in a crystalline form. Silver thus obtained is never free from traces of copper.

Pure silver can be obtained by fusing the pure chloride with sodium carbonate. The reaction is shown in the equation:



Owing to the copious evolution of carbon dioxide which takes place during the decomposition, some of the silver may be thrown from the crucible, and loss may occur by the absorption by the crucible of some of the fused chloride. To

avoid this the sides of the vessel should be coated with a hot saturated solution of borax.

A mixture of 100 parts of argentic chloride, 70.4 of calcium carbonate (chalk), and 4.2 of charcoal has been recommended as a means of obtaining pure silver. This mixture is heated to dull redness for thirty minutes, and then raised to full redness; carbon dioxide and carbon monoxide are given off; the calcium chloride is converted into calcium oxychloride, underneath which, in the bottom of the crucible, will be found the button of pure silver.

Electrolytic processes are also used and the nature of the deposit of silver is dependent upon the acid radicle present in the solution. The pyrophosphate gives a crystalline deposit of silver, while the nitrate radicle produces a black powder.

Properties.—Silver is a pure white metal having a perfect metallic luster. The color of silver is taken as the type for the color of white metals and these metals are spoken of as silvery white in color. It is harder than gold and softer than copper. The specific gravity of silver is about 10.42. Silver is the best conductor of heat and electricity and the conductivity of other metals is generally compared with that of silver. The melting point, as determined by Becquerel, is 960° C., but the more recent determination Berthelot places the fusing at 962°. Upon solidification silver forms crystals belonging to the isometric system and the latent heat of fusion is 21.07 calories. At about 1955° C. silver volatilizes, yielding a green vapor and can be distilled by means of the oxyhydrogen blow-pipe. Thin films of silver appear blue by transmitted light.

If ferric citrate be added to the silver nitrate, a red solution and lilac precipitate of free silver can be made. The latter after washing with ammonium nitrate gives a red solution in water. The silver is present in a very finely divided state and is known as "colloidal" silver.

If mercury be added to a solution of silver nitrate a precipitate of metallic silver will be formed in a short time, resembling real vegetation, this is called the "silver tree."

Nearly all of the metals precipitate metallic silver from a solution of its salts.

Many different methods have been used to whiten the surface of silver objects, Gee's method of whitening consists in making the silver red hot, and then boiling in 2.5 per cent. solution of sulphuric acid.

Silver articles are sometimes finished with what is called the oxidized finish. There are two distinct shades in use, one produced by a chloride, which has a brownish tinge, and the other by sulphur having a bluish-black tint. The following is said to produce a very fine bluish-black tint. The silver piece is washed with a solution containing copper sulphate, ammonium chloride and acetic acid. The article is then warmed and placed in a warm solution of either sodium or potassium sulphide.

In the molten state silver absorbs twenty-two times its volume of oxygen and during solidification the gas is expelled, causing the formation of small blisters; this is spoken of as the spitting of silver. The spitting of silver may be entirely prevented by the admixture of small quantities of copper, bismuth, or zinc to the silver.

Silver is not acted upon by atmospheric oxygen, but is quickly tarnished by traces of hydrogen sulphide in the air. The blackening of silver in air may be prevented by coating the silver with collodion diluted with alcohol. To remove the tarnish, potassium cyanide or sodium hyposulphite solutions may be used. It is claimed that silver utensils darkened from use may be brightened by boiling in a bright aluminum vessel with soapy water.

In malleability silver ranks second to gold, and in ductility is exceeded by gold and according to later experimentation, platinum. There is no scientific foundation to the ranking of metals according to malleability and ductility, and the tables given upon these properties are for the purpose of *simply* giving the student some idea of malleability and ductility. As our methods of determining these properties are improved upon, there is no question but that these tables will be very greatly altered.

Compounds.—Silver forms one oxide corresponding to the formula Ag_2O , although two other oxides, Ag_2O_2 and Ag_4O , are believed to exist.

Silver monoxide, Ag_2O , is obtained by adding sodium or potassium hydroxide to a solution of silver nitrate. A brown precipitate consisting of hydrated oxide is found, which when heated is converted into the anhydrous compound. When the carbonate is heated to 200° this oxide is also found.

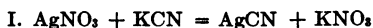
Upon heating silver monoxide to 260° it begins to reduce with the liberation of oxygen and metallic silver. These reactions characterize silver as a noble metal.

When silver oxide dissolves in ammonia a very explosive compound, fulminate of silver, is found, and is believed to have the formula AgN_3 .

Silver chloride, AgCl , is a white, curdy precipitate produced when a soluble chloride is added to silver nitrate. It melts at 451° to a yellowish liquid which congeals to a horny mass. When exposed to light this compound darkens, assuming a violet tint, and finally becoming dark brown. This compound is used in photography.

Silver nitrate, AgNO_3 , is obtained by dissolving silver in nitric acid. It forms large, colorless, rhombic crystals which melt without decomposition at 218° . This is a very important compound and is used in dentistry because of its therapeutic effect. It is also used whenever a soluble silver salt is desired.

Silver Cyanides, AgCN .—This compound is prepared by adding potassium cyanide to a solution of silver nitrate. Two conditions are met with, depending upon the quantity of cyanide used.



This reaction takes place when only a small quantity of cyanide is added, and silver cyanide, being insoluble, precipitates from the solutions.

When an excess of potassium cyanide is added, the following is formed:



This silver potassium cyanide is used in eletroplating. The double salt breaks down and the silver is deposited as a uniform metallic coating.

Solubilities.—The fixed alkalies do not attract silver, hence silver crucibles are used instead of platinum for fusion with caustic alkalies.

Ammonium hydroxide dissolves finely divided silver, in the presence of air. Nitric acid, both dilute, and concentrated, dissolve silver readily. Dilute sulphuric is without action upon it except when the silver is in the finely divided state. Hot concentrated sulphuric acid dissolves silver with the formation of silver sulphate, sulphur dioxide and water. Hydrochloric acid is without action upon it, but the metal is readily attacked by chlorine, bromine, or iodine. Silver is soluble in potassium cyanide in the presence of air:



From this solution the silver may be again precipitated by heating with metallic zinc, lead or hydrochloric acid. The "cyanide process" for the recovery of gold and silver is based upon this reaction.

Alloys.—At ordinary temperatures mercury and silver unite very slowly but upon heating the two unite much more readily. Another method of preparation is by treating a solution of silver nitrate with mercury. This causes the silver to be precipitated in a finely divided state and then upon shaking the amalgam is formed. Several compounds are said to be formed.

Copper and Silver.—The two metals are miscible in all proportions in the fluid state and it requires heating for some time before the mass becomes homogeneous. Fenchel states that an alloy containing 2 per cent. of silver with copper, shows free silver after being kept fluid for ten hours. Alloys containing 96 or 97 per cent. of silver are found to be homogeneous after eight to ten hours' heating. Copper is alloyed with silver to increase the hardness of the latter metal, this prevents the loss of silver by attrition. Coin silver contains from 900 to 925 parts of silver to the 1000,

and from 75 to 100 parts of copper. Standard silver is silver so alloyed.

The following is a list of the proportions of copper and silver in the silver (coin) of some of the nations:

United States	silver 900, copper 100
France	" 900, " 100
England	" 925, " 75
Indian rupees	" 947, " 53
German-Prussian thalers	" 811, " 187
Prussian silver groschen	" 283, " 717

Gold and silver readily alloy and Fenchel states that the fusing point of gold is hardly lowered even by the addition of silver up to 50 per cent. The tensile strength of gold is increased by alloying with silver. Gold-silver alloys are soluble in boiling sulphuric acid, the silver dissolving, leaving the gold unchanged; when the proportion of gold to silver is not greater than 4 to 7 in an alloy nitric acid dissolves the silver and the gold remains unchanged.

Platinum and Silver.—Platinum and silver alloy and the fusing point depends upon the percentage of platinum present. An alloy of these two metals, say 10 per cent. platinum, may be prepared by melting the silver and then adding platinum in the form of a thin ribbon. The alloy thus prepared should be heated for some time to ensure perfect mixture of the two metals. Dental alloy, used to some extent in Europe for the construction of dental bases, contained from 25 to 30 per cent. of platinum with silver. The object of alloying the platinum with silver is to increase the resistance of silver to the action of chemicals. These alloys containing 10 per cent. of platinum are attacked by nitric acid and both platinum and silver are dissolved. Sulphur also attacks this alloy-forming sulphide of silver. At the present market price of platinum, there is no occasion for the use of this alloy.

Lead and Silver.—Lead is miscible with silver in almost all proportions, and because of the ready alloying of these two metals lead is used to dissolve silver from its ores in the process of assaying. The old saying is "that all lead contains silver" is for the most part true, and in test—lead used in the

above process (assaying)—allowance must always be made for the silver already present in the lead. Zinc alloys readily with silver and these two metals seem to have more of an affinity for each other than lead has for silver. The Parker's process of desilverizing lead proves this statement. Zinc will prevent lead from spitting and also interferes with the oxidation of other metals when alloyed with silver.

Silver Solders.—Silver solders are used to solder German silver, brass, copper, silver and silver alloys. Silver solders are classed as hard solders because they require red heat to fuse. They consist of alloys of silver, copper and zinc.

Richardson's *Mechanical Dentistry* gives the following formulas for these solders:

No. 1.

Silver	66 parts
Copper	30 "
Zinc	10 "

No. 2.

Silver	6 pennyweights
Copper	2 "
Brass	1 "

No. 3.

Silver	5½ pennyweights
Brass	40 grains

Dr. Kirk recommends the following compositions:

Fine silver.	Copper.	Brass.	Zinc.
4.0	..	3.0	
2.0	..	1.0	
19.0	1.0	10.0	5
66.7	23.3	..	10
50.0	33.4	16.6	
11.0	..	4.0	1

Van Eckart's alloy, employed to some extent in France as a base for artificial dentures, is composed of the following proportions: silver, 3.53; platinum 2.40; and copper 11.71. It is very elastic (which property it does not lose by annealing) and can be highly polished.

RESUMÉ.

Symbol, Ag.	Specific gravity, 10.42 to
Valency, 1.	10.52.
Atomic weight, 107.88.	Crystalline form, isometric.
Melting point, 964° C.	Chief ore, horn silver.
Specific heat, 0.057.	Conductivity of electricity, 1st.
Malleability, 2d.	Conductivity of heat, 1st.
Tenacity, 4th.	Coefficient of expansion,
Color, white.	0.00001909.
Boiling point, 1955° C.	Ductility, 2d.

CHAPTER X.

BISMUTH.

Symbol, Bi. Atomic weight, 208.

Occurrence.—Bismuth occurs for the most part in the native state. The native metal is often alloyed with arsenic or impure with sulphur or tellurium. Native bismuth occurs in crystalline rocks, and clay slate associated with ores of cobalt, nickel, gold, lead and zinc, also with molybdenite, wolframite and scheelite. Bismuth is found intimately mixed with other minerals, as with tin ore in Bolivia; Cobalt in Saxony and gold-bearing iron ore in Queensland, Australia.

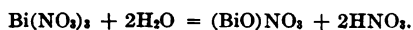
The principal localities from which the native metal is obtained are the following: Saxony and Bohemia, Chili, Sweden, Norway and Australia. The native metal is not found in any quantities in the United States, however, some is obtained from South Carolina.

Other ores of bismuth are: bismuthite or glance, sulphide, Bi_2S_3 . Telluride, carbonate and bismuth oxide, Bi_2O_3 .

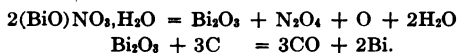
Bismuth is one of the comparatively rare, useful metals; and its commercial value is generally at least ten times the cost of antimony.

Reduction.—*Native Metal.*—In refining the native metal the ore is broken up and liquated by being heated in inclined pipes, when the bismuth readily melts and drains off from the earthy impurities. As obtained from this process the bismuth contains impurities, and in order to obtain pure bismuth, wet methods must be used.

The impure metal is dissolved in nitric acid forming $\text{Bi}(\text{NO}_3)_3$, and then precipitated by the addition of water.



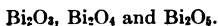
The basic nitrate is next dried and heated in a crucible with charcoal; the salt is first converted into the trioxide Bi_2O_3 by the action of heat and then reduced by the carbon:



The method made use of in Saxony, where most of the bismuth of the world is produced, the ores are first roasted to free them from sulphur, arsenic and other volatile constituents. After they are roasted they are smelted in crucibles with iron, charcoal and slag, the melted bismuth settling out in the bottom of the crucible; or the roasted ore may be treated with strong hydrochloric acid which dissolves the impure bismuth and from which it is precipitated as oxychloride by the addition of water. The metal may be further purified electrolytically.

Properties.—Bismuth is a lustrous white metal, with a faint reddish tinge, it closely resembles antimony in appearance; however, antimony is a white metal, and bismuth when compared with antimony shows a distinct reddish cast. It is hard and so brittle that it may readily be ground to a powder in a mortar. Bismuth may be said to be devoid of malleability and ductility. It is also a poor conductor of heat and electricity. Bismuth is unacted upon by dry air or oxygen. The melting point of bismuth is 270°C. , and its specific gravity 9.82. It expands upon solidification and imparts low fusing properties to its alloys; however, it also makes the alloys more or less brittle. Small quantities of bismuth renders gold and silver brittle when alloyed with them and also reduces the conductivity of copper. Rhombohedral crystals of bismuth may be obtained when the metal is fused and allowed to cool slowly; these crystals form at the edges of the metal and may be obtained by decanting the still fused portion of the metal. Its position in the electro-motive series is between copper and silver and it therefore inclines toward the noble metals.

Compounds.—Bismuth is said to form three oxides:



Bismuth dioxide is a pale yellow powder and when treated with sulphuric acid, bismuth and bismuth sulphate are formed.

Bismuth trioxide is the most important oxide and when the two remaining oxides are heated in air the trioxide is formed. It is a light yellow powder, readily fusible, forming a vitreous mass on cooling.

Bismuth tetroxide, Bi_2O_4 , is possibly a mixture of Bi_2O_3 and Bi_2O_5 ; $\text{Bi}_2\text{O}_3 + \text{Bi}_2\text{O}_5 = 2\text{Bi}_2\text{O}_4$.

Bismuth hydroxide, $\text{Bi}(\text{OH})_3$, is formed by precipitating a bismuth salt with the alkali hydroxides; upon drying $\text{Bi}(\text{OH})_3$ forms the oxyhydroxide $\text{BiO}(\text{OH})$.

Bismuth trichloride is prepared by passing dry chlorine gas over powdered bismuth, gently heated in a retort. When this salt is treated with water a precipitate of BiOCl , bismuth oxychloride is formed. The formation of this compound is a means of identifying bismuth in solution.

Bismuth nitrate is prepared by dissolving bismuth in nitric acid.

The subnitrates represented by various formulas may be prepared from the nitrate by adding much water to the solution of the salt.

Solubilities.—The best solvent for bismuth is nitric acid; hydrochloric acid is without action upon it. Conc. sulphuric dissolves bismuth with the evolution of sulphur dioxide. When placed in chlorine it unites with it, with the evolution of light.

Alloys.—Bismuth is said to form an adhesive mass with mercury, which contracts upon setting.

Low Fusing Alloys.—These alloys are used as safety plugs in automatic sprinklers and also in dentistry to construct dies for crown and bridge-work.

Wood's metal is composed of bismuth 4, lead 2, tin 1, and cadmium 1 part; fusing point, 60.5°C .

Rose's metal: bismuth 2, lead 1, and tin 1 part; melting point, 93.75°C .

Lichtenberg's metal: bismuth 5, lead 3, tin 2 parts; melting point, 91.6°C .

Mellotes (Newton's) metal: bismuth 8, lead 5, tin 3 parts; melting point, 94.50° C.

RESUMÉ.

Symbol, Bi.	Specific gravity, 9.82.
Valency, III or V.	Crystal form, rhombo-
Atomic weight, 208.	hedral.
Melting point, 270° C.	Chief ore, native bismuth.
Boiling point, 1420° C.	Conductivity of heat, 18.
Color, reddish tinge.	Conductivity of electric-
Specific heat, 0.0308.	ity, 1.22.
Ductility and malleability,	Coefficient of expansion,
brittle.	0.000013.

CHAPTER XI.

COPPER.

Symbol, Cu (Cuprum). Atomic weight, 63.57.

Occurrence.—Copper is found in the native state in various localities, notably in the Lake Superior region. In combination copper is a very abundant element and is widely distributed. The most important ores are the following:

Ruby ore, Cu_2O ; copper glance, Cu_2S ; copper pyrites, $\text{Cu}_2\text{SFe}_2\text{S}_3$; purple copper ore, Cu_3FeS_3 ; malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; azurite, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$.

Historical.—Copper has been known to mankind from the earliest ages, and probably in the form of bronze was the first alloy made use of.

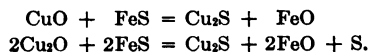
Reduction.—The method of reduction depends upon the ore used; the carbonate and oxide may be reduced by smelting the ore in a blast furnace and then reducing with coke or coal, according to the reaction:



In the case of mixed ores containing sulphides, the process consists of six distinct stages:

1. The ores containing on an average 30 per cent. iron and 13 per cent. copper, are first calcined; usually in a reverberatory furnace (Fig. 45); the sulphur is burned to sulphur dioxide and the metals are partially oxidized.

2. Fusing the calcined ore in a furnace (Fig. 46) when the copper oxides formed during the calcination react upon a portion of the ferrous sulphide, with the formation of cuprous sulphide and ferrous oxide:



The oxide of iron combines with the silica present to form a fusible silicate of iron or slag which contains little or no

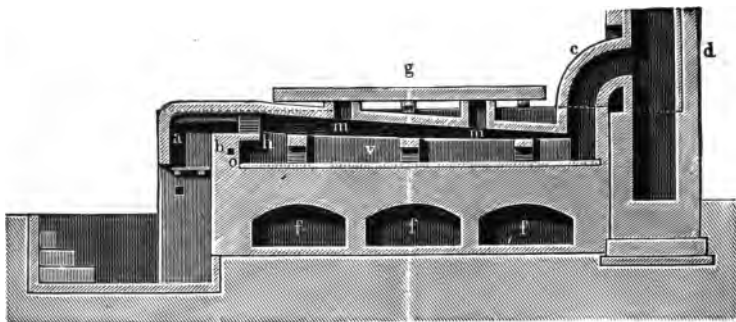


FIG. 45

copper. This is run off, leaving a regulus containing 30 to 35 per cent. copper and known as course metal consisting of

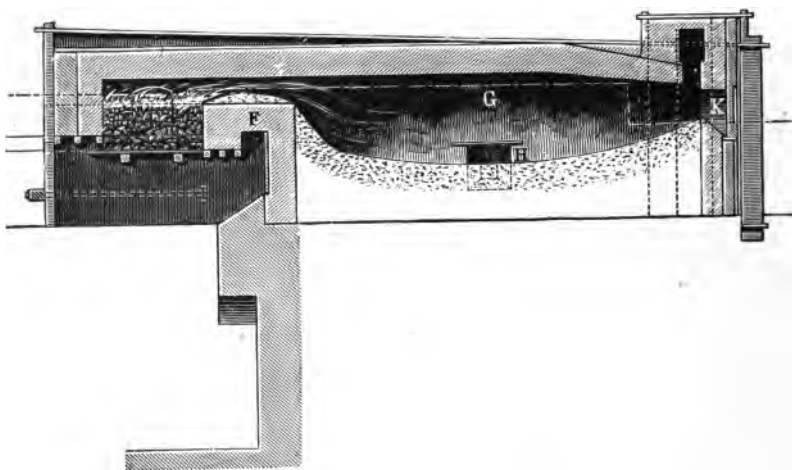


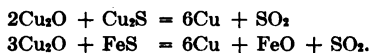
FIG. 46

cuprous and ferrous sulphides. The course metal is granulated by allowing it to flow into water.

3. The granulated course metal is again calcined, which results in the oxidation of more of the sulphur as the dioxide, and the dioxide and the partial oxidation of more of the metals.

4. The calcined mass is then fused with some refinery slag, which results in the production of a regulus consisting of nearly pure cuprous sulphide, the greater part of the iron having passed into the slag. The regulus, called fine-metal or white-metal, contains 60 to 75 per cent. copper.

5. This operation consists of roasting the white-metal in a reverberatory furnace. A portion of the cuprous sulphide is reduced to cuprous oxide, and as the temperature rises reacts upon another portion of cuprous sulphide. The reactions which occur in this step are as follows:



The metallic copper thus obtained has a blistered appearance and is known as blister-copper.

The impure copper is melted down upon the hearth of a reverberatory furnace in an oxidizing atmosphere. The impurities present such as iron, lead, and arsenic are first oxidized in a suitable furnace represented in Fig. 47, and the oxides are either volatilized or combine with the siliceous matter to form a slag. The oxidation is continued until the copper begins to oxidize; when the oxide thus formed reduces any cuprous sulphide present with the evolution of sulphur dioxide. Finally the oxide of copper present is reduced with coal and stirred with poles of wood.

Wet Process.—Copper present in burned pyrites obtained from the manufacture of sulphuric acid, which may contain 3 per cent. copper, are subjected to a smelting process. When this material is smelted with 12 to 15 per cent. of common salt, the copper is converted into cupric chloride. The mass is treated with water, the cupric chloride dissolves, and metallic copper can be precipitated by means of scrap-iron, or by electrolysis.

Electrolysis.—Copper may also be reduced by electrolysis, but the expense entailed is too great in most cases. When a high grade of purity is demanded, this process may be used and a grade of copper containing about 0.02 part in a thousand may be obtained.

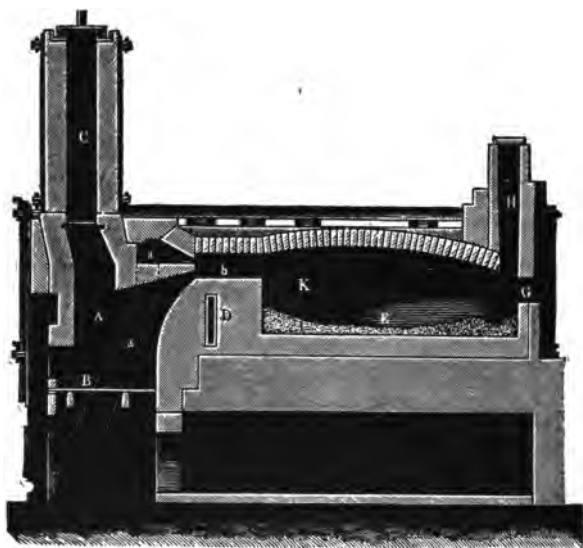


FIG. 47

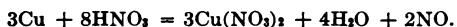
Properties.—Copper is a lustrous metal having a reddish-brown color. The native metal is found crystallized in regular octahedra, and small crystals of the same kind may be obtained by the slow deposition of the metal from solution by reducing agents. On account of its chemical resistibility, its good mechanical properties, and its melting point, copper is largely used for utensils of all kinds. Another great sphere for the application of copper depends upon its great conductivity for the electric current. In this respect it is only exceeded by silver. For this purpose it must be in the pure condition, as small quantities of impurities lessen its conductivity.

Copper is an extremely tough metal and can be readily rolled into sheets or drawn into wire. It ranks fourth in malleability, fifth in ductility, and second in tenacity. As a conductor of heat and electricity it ranks second to silver. Its melting point is about $1050^{\circ}\text{C}.$, and its boiling point, $2310^{\circ}\text{C}.$ Copper possesses the property of absorbing gases, among which may be mentioned carbon monoxide, sulphur dioxide and hydrogen. Oxygen is absorbed in the same manner as silver and forms bubbles upon the surface of the cast copper. The molten metal dissolves cuprous oxide while fusing and this tends to affect the physical properties of the metal. Copper is only slowly acted upon by exposure to dry air, but in the presence of atmospheric moisture and carbon dioxide, it becomes coated with a greenish basic carbonate. When volatilized in the electric arc, copper gives an emerald-green vapor. Copper leaf transmits greenish-blue light. Solutions of copper are reduced to the metallic state by Zn, Cd, Al, Pb, Fe, Co, Ni, Bi, Mg. A bright strip of iron in solution of cupric salts acidulated with hydrochloric acid, receives a bright copper coating, recognizable from solutions in 120,000 parts of water.

Arsenic in small quantities has no injurious effects upon copper unless the percentage is 1 per cent. or over, then the copper becomes brittle when rolled at an elevated temperature.

Antimony in small quantities does not affect the ductility of copper. Copper containing 0.529 per cent. of antimony can be drawn into the finest wire just as well as pure copper. However, both arsenic and antimony, present to a few thousandths of 1 per cent., affect the conductivity of electricity of copper.

Solubilities.—Copper does not dissolve readily in acids with the evolution of hydrogen. It dissolves most readily in nitric acid, chiefly with the evolution of nitric oxide:



With hot concentrated sulphuric acid, sulphur dioxide is evolved:



Dilute hydrochloric and sulphuric acids are without action upon copper when air is excluded, but slowly attack it in the presence of air or a catalytic agent, such as platinum. Finely divided copper is soluble in boiling concentrated hydrochloric acid. In the presence of air, copper is acted upon by ammonia, forming a deep blue solution. Water dissolves copper from a polished copper surface and it is found that the water has been sterilized by the copper in solution.

Compounds.—Copper forms two classes of compounds: cuprous with a valency of *one* and cupric having a valency of *two*. The cuprous compounds are very unstable.

Cuprous oxide, Cu_2O , occurs native as red copper ore. It may be prepared in the wet way by heating cuprous chloride with sodium carbonate in a crucible. Cuprous oxide fuses at red heat and when melted with glass imparts a rich ruby red color. Cuprous oxide occurs in the rare mineral tenorite. It is formed when copper is heated in air or oxygen. This compound of copper is extensively used in chemistry because of its oxidizing power. In dentistry it is used in black copper cements. Cupric hydroxide is a pale blue precipitate formed when sodium or potassium hydroxides are added to a solution of a copper salt. If the precipitate is boiled, a black basic oxide of copper is formed. If ammonium hydroxide is added to a soluble copper salt the hydroxide is first precipitated; this dissolves in an excess of ammonium hydroxide, resulting in the production of a blue solution, copper sulphate; blue vitriol is formed by dissolving the metal or its oxide in sulphuric acid. This salt is used in the preparation of voltaic cells, and is also used in medicine.

Sulphides.—Two sulphides are known: cuprous, Cu_2S , and cupric, CuS . Cuprous sulphide occurs in nature as copper glance, in the form of gray metallic-looking rhombic crystals. It may be prepared in the dry way by burning copper in sulphur vapor. Cupric sulphide occurs in nature as indigo-copper. It may be prepared in the dry way by heating copper or cuprous sulphide with sulphur to a temperature not above 114° ; so obtained the compound is

blue. In the wet way hydrogen sulphide precipitates it from solutions of cupric salts; it is a black precipitate.

Alloys.—Copper amalgam was used to a considerable extent at one time in dentistry; however, at the present time it has gone into disuse and only occasionally it is of service to the dentist. It may be prepared by pouring pure mercury into a beaker containing copper sulphate and then stirring with an iron rod. An amalgam known as Sullivan's amalgam is prepared as follows: pure copper is obtained in a finely divided state by boiling a concentrated solution of copper sulphate with distilled zinc until the color of the salt disappears, when the zinc is removed. The pulverulent mass of copper in the bottom of the vessel is washed with dilute sulphuric acid and then with distilled water and dried. The copper is then treated with a solution of mercuric nitrate until it becomes coated with mercury. The mercury is then added to the extent of about twice the weight of copper. It is then rolled into small lozenge-shaped pieces which become quite hard. This amalgam possesses the property of softening with heat and again hardening, and when employed as a filling material one of the lozenge-shaped pieces is placed in a small iron spoon and heated over the flame of a spirit lamp until small globules of mercury are driven to the surface, when it is placed in a small glass or porcelain mortar and rubbed into a smooth paste. Some recommend washing with a weak solution of sulphuric acid, or soap and water, and lastly with clean water alone, to remove the last traces of either acid or soap, and finally squeezing through chamois-leather, to exclude surplus of mercury, when it is ready to be introduced into the cavity. It requires several hours to harden. Mr. Fletcher says of this amalgam that "it is an absolutely permanent filling, as the copper salts permeate and perfectly preserve the tooth." It is said to be quite insoluble in the mouth. It, however, becomes intensely black, and imparts a most objectionable stain to the teeth.

Copper and iron form no true alloy, but when these two metals are mixed the copper is found irregularly distributed throughout the mixture.

Tin alloys with copper and diminishes the malleability; this effect is produced even when tin is present to the extent of 1 per cent. or over.

Zinc and copper, forming brass, diminishes the malleability when hot.

Lead and copper are miscible in all proportions, but the greater part of the lead may be liquated from the alloy by gentle heating. In small quantities it does not interfere with malleability.

Bismuth renders copper unworkable and a few thousandths of 1 per cent. interferes with its conductivity.

Silver and copper are alloyed for the purpose of coinage.

Gold and copper are also used for coinage; the copper is added to increase the hardness of the gold.

Platinum and palladium alloy with copper in certain proportions; the first forms an alloy resembling gold in color, while the latter resembles brass.

Aluminum bronze consisting of aluminum and copper, and containing from 1 to 10 per cent. aluminum, resembles gold in color and is very resistant to the action of solvents. It is also malleable and ductile. This alloy has been used for orthodontic appliances.

The following are among the most important alloys of commerce:

English brass	copper, 2 parts; zinc,	1 part.
Dutch brass (Tombac)	copper, 5 parts; zinc,	1 part.
Muntz metal	copper, 3 parts; zinc,	1 part.
Gun metal	copper, 9 parts; tin,	1 part.
Aluminum bronze	copper, 9 parts; aluminum, 1 part.	

RESUMÉ.

Symbol, Cu.	Boiling point, 2310° C.
Valency, I or II.	Specific gravity, 8.8 to 8.9.
Atomic weight, 63.57.	Crystalline form, isometric.
Melting point, 1150° C.	Conductivity of electricity, 2d.
Specific heat, 0.0968.	Conductivity of heat, 2d.
Malleability, 4th.	Coefficient of expansion,
Tenacity, 2d.	0.000017182.
Color, pink.	Ductility, 5th.

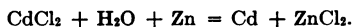
CHAPTER XII.

CADMIUM.

Symbol, Cd. Atomic weight, 112.4.

Occurrence.—The only cadmium mineral is the sulphide greenockite (CdS). The principal source is from zinc ores which contain from 1 to 3 per cent.; and in the process of extracting zinc the cadmium is obtained in the first portions of the product of the distillation, partly as metal and partly as oxide.

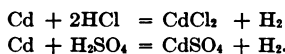
Reduction.—The crude product as obtained from the calcination, reduction, and distillation of zinc ores, is dissolved in dilute sulphuric or hydrochloric acid and the cadmium precipitated as the sulphide with hydrogen sulphide. The cadmium sulphide is then dissolved in strong hydrochloric acid and precipitated as carbonate, by means of ammonium carbonate. The washed and dried carbonate is first converted into the oxide, and finally mixed with charcoal and distilled. A second process consists in redistilling the crude metal obtained from the distillation of zinc, and then dissolving in hydrochloric acid, then precipitating from solution by means of zinc plates.



Properties.—Specific gravity, liquid, 7.986; cooled, 8.67; hammered, 8.6944; melting point, 320.6°C., 608° F.; boiling point between 772° and 763° C.; specific heat, 0.0567. It is a bluish-white metal resembling zinc in appearance but much more malleable and ductile. It tarnishes superficially on exposure to air, and when strongly heated burns with the formation of a brown vapor of cadmium oxide, CdO. Cadmium is a soft metal, harder than lead, but softer than tin or zinc. Conductivity, somewhat less than zinc. More tenacious than tin. At a temperature of 80° C. cadmium becomes very brittle, and upon bending it emits a sound

similar to the cry of tin. It may be distilled in a current of hydrogen above 800° , forming silver-white crystals belonging to the regular system. Cadmium is less electropositive than zinc, and is precipitated in the metallic condition, from its solutions, by that metal. It precipitates Au, Pt, Ag, Hg, Bi, Cu, Pb, Sn, and Co, and is precipitated itself by zinc, Mg, and Al.

Solubilities.—Cadmium dissolves slowly in hot, moderately dilute hydrochloric and sulphuric acids, with the evolution of hydrogen:



Alkalies are said to dissolve it. Cadmium is readily soluble in nitric acid with generation of nitrogen oxides. Cadmium oxide, formed when cadmium burns in air, is brown in color, and may also be obtained by heating the nitrate or carbonate. Cadmium and silver are miscible in all proportions and three compounds are formed. The fusing point of cadmium is only slightly raised by the addition of small quantities of silver, according to the experiments of Petrenko and Fedorov.

Uses.—Cadmium is used in low fusing alloys; unlike bismuth, the cadmium alloys are not brittle. Some of these alloys fuse below the boiling point of water; they may be hammered or rolled but are not so crystalline in structure as the bismuth alloys.

	Cd.	Pb.	Sn.	Bi.	Melting points.
Wood's metal	2	4	2	5	$160^{\circ}\text{ F.}, 71^{\circ}\text{ C.}$
Lipowitz	3	8	4	15	$158^{\circ}\text{ F.}, 65^{\circ}\text{ C.}$
Molyneaux's alloy . .	2	3	2	5	60° C.
Crouse's alloy	1	5	3	8	79° C.
Lichtenberg's alloy . .	2	13	7	7	75° C.

RESUMÉ.

Symbol, Cd.	Boiling point, 756° C.
Valency, II.	Specific gravity, 8.6.
Atomic weight, 112.4.	Chief ore, greenockite.
Melting point, 320.6° C.	Conductivity of electricity, 159.
Specific heat, 0.0567.	Coefficient of expansion,
Malleability, 5th.	0.000012.
Color, bluish white.	Ductility, 11th.

CHAPTER XIII.

ANTIMONY.

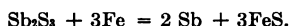
Symbol, Sb (stibium). Atomic weight, 120.4.

Historical.—Antimony has been known from antiquity. Jeremiah speaks of it (Stibick stone), being used to blacken the eyebrows, or as a cosmetic. The Romans used a chalice lined with antimony, placing sour wine into it and allowing it to stand overnight. The contents was drunk after a night of debauching and the tartar emetic formed would produce its characteristic effects, relieving the distress of the person partaking of the draught.

Occurrence.—Lead ores sometimes contain antimony. The sulphide stibnite, Sb_2S_3 , is the chief ore. It also occurs as the native metal containing arsenic, iron and silver as impurities. There are also natural occurring oxides, valentinite, Sb_2O_3 , antimony ochre, Sb_2O_4 , but they are found only in small quantities. France, Italy, Mexico and Japan are the chief producers of antimony.

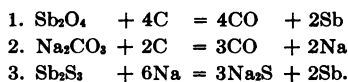
Reduction.—Antimony may be reduced from the sulphide by one of the following processes:

1. The crushed ore is heated in plumbago crucibles with scrap iron. The mass melts and the sulphur combines with the iron, forming iron sulphide and liberating the antimony which settles beneath:



2. The crude antimony is freed from earthy impurities by melting, the antimony sulphide is then drawn off from the impurities. The purified ore is mixed with about one-half its weight of charcoal, to prevent caking, and carefully roasted. The antimony is partially converted into the oxide, a portion of which volatilizes and collects in the flues. The arsenic present is also oxidized and collects with the oxide of antimony, while the sulphur passes off as a sulphur dioxide. The

antimony ash remaining in the furnace, consisting of the oxide and unchanged antimony sulphide, is mixed with charcoal and sodium carbonate and heated to redness in a crucible.

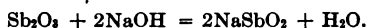


The metal as obtained by this process must be subsequently refined. The impurities commonly present are sulphur, copper, iron, arsenic, silver and gold. The metal may be refined by fusing with sodium carbonate and a little sulphide of antimony, followed by two fusions with sodium carbonate alone. Liebig's process consists in fusing the impure antimony with sodium carbonate, potassium carbonate and a little antimony sulphide.

Properties. — A very brittle tin-white metal, usually massive, with fine, granular, steel-like texture. It is very low in malleability, tenacity, and ductility; hardness about 3 to 3.5; specific gravity, 6.5 to 6.7; melting point, 425° C., 797° F.; boiling point, between 1090° and 1450° C., specific heat, 0.0513. It is but little tarnished in dry air and oxidizes but slowly in moist air, forming a mixture of antimonous oxide and antimony which is of a blackish-gray color. At red heat it burns in air with incandescence, forming white antimonous oxide. In the act of solidification, antimony expands; it imparts this property to its alloys, thus giving to them the valuable property of taking very fine and sharp lines in casting. It is a very poor conductor of heat and electricity and is a diamagnetic in its behavior toward the magnet. The powdered metal unites with chlorine gas, taking fire spontaneously and forms the trichloride SbCl_3 . Antimony may be obtained in the amorphous form by the electrolysis of a solution of tartar emetic. This form of antimony has the appearance of a smooth, polished rod of graphite. Amorphous antimony is very unstable and the slightest disturbance will cause it to change, with explosive violence, to the crystalline form.

Oxides. — Antimony forms three oxides: Sb_2O_3 , Sb_2O_4 , and Sb_2O_5 .

Antimonous oxide, Sb_2O_3 , is formed: (1) when dilute nitric acid acts upon Sb; (2) by treating antimonous chloride, SbCl_3 , with Na_2CO_3 or NH_4OH ; (3) by heating Sb_2O_4 or Sb_2O_5 to 800° . It is a white powder which turns yellow on heating and again becomes white upon cooling. It melts at red heat, becomes crystalline upon cooling. Antimonous oxide sometimes acts as an acid, with sodium hydroxide it reacts as follows:

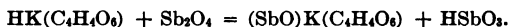


But under most conditions it acts as a basic oxide.

Antimony tetroxide, Sb_2O_4 , is formed when antimony burns in air. It may be prepared by strongly heating antimony pentoxide;



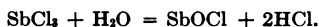
Antimony tetroxide is a white, non-volatile powder which is insoluble in water. It is decomposed by boiling hydrogen potassium tartrate, cream of tartar forming tartar emetic:



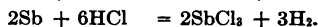
Antimony pentoxide, Sb_2O_5 , is obtained by treating antimony with strong nitric acid and heating the antimonous acid formed to 275° . It is a straw-colored powder, insoluble in water; when heated to 300° it is converted into Sb_2O_4 . It possesses feeble acid properties; when fused with sodium carbonate, sodium metantimonate is formed:



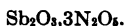
Antimony salts in solution readily form basic salts and are thus precipitated from solution; however, in the presence of acids this reaction will not occur.



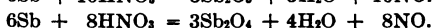
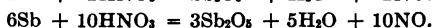
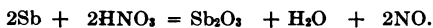
Solvents.—Dilute hydrochloric and sulphuric acid are without action upon antimony. The concentrated acids convert it into the sulphate and chloride respectively.



Dilute nitric acid attacks antimony with the formation of Sb_2O_3 or a compound of the oxide with nitrogen pentoxide:



Concentrated nitric acid oxidizes the antimony chiefly into the tetroxide and pentoxide.



Aqua regia attacks antimony with the formation of the trichloride SbCl_3 , but if sufficient nitric acid be present this is rapidly changed to antimony pentachloride, SbCl_5 ; however, if too much nitric acid is present, the corresponding oxides are formed.

Alloys of Antimony.—Antimony increases the hardness of metals when alloyed with them. It causes expansion in most alloys and is used in type metal. With the noble metals it renders them brittle and thus destroys their malleability and ductility.

Amalgam of antimony is soft and readily decomposes.

Gold.—Antimony destroys the malleability of gold.

Tin.—Antimony increases the hardness of tin but renders it brittle.

Type metal consists of lead, 50; antimony, 25; tin, 25. Copper is sometimes added to some varieties.

Antifriction metal is made by alloying copper, antimony, and tin in various proportions. Other varieties contain lead, antimony and tin.

Britannia metal is an alloy of tin, antimony, copper, zinc, and bismuth; it is used in making spoons resembling silver.

RESUMÉ.

Valency, III or V.

Atomic weight, 120.2.

Melting point, 425° to 632° C.

Boiling point, 1440° C.

Specific heat, 0.0513.

Color, bluish white.

Specific gravity, 6.8.

Malleability, brittle.

Ductility, brittle.

Chief ore, stibnite.

Crystalline form, rhombohedral.

Conductivity of heat, 40.

Conductivity of electricity, 4.5.

Coefficient of expansion, 0.000017.

CHAPTER XIV.

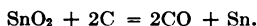
TIN.

Symbol, Sn (stannum). Atomic weight, 119.

Occurrence.—Tin occurs as the oxide cassiterite or tin-stone, SnO_2 , which is the principal ore. It is also found in small quantities as the sulphide, in the mineral stannite $(\text{CuSnFe})\text{S}$. The ores of this metal are found in primitive rocks, generally in granite either in veins or beds, and often associated with copper and iron pyrites. The East Indian settlements of Malacca, Banca and Belitong are the greatest producers of tin-stone. It is also found in Australia, England, Mexico and various localities in the United States.

Historical.—Tin has been known from the earliest of times, being used in the construction of bronze. The Phœnicians traded with England for this article for more than 1100 years before the Christian Era.

Reduction.—In the reduction of tin-stone the process ordinarily consists of three operations, namely: (1) Calcining; (2) washing; (3) reducing or smelting. If the ore is free from impurities as it is occasionally found (stream-tin), it may be smelted at once. The ore is washed to free it from earthy matters, then finely crushed. It is next placed in a reverberatory furnace and calcined. Sulphur and arsenic pass off as sulphur dioxide and arsenious oxide, and the arsenic deposits in the flues. The iron and copper are oxidized to oxide and sulphate. The calcined ore is next washed, whereby copper sulphate is dissolved and the iron oxide and other lighter matters are removed. The purified ore is then mixed with powdered coal and smelted in a reverberatory furnace:



The tin usually contains lead, iron, arsenic, antimony and copper. The metal so obtained is purified by first heating

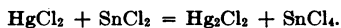
it upon the hearth of a similar furnace until the more readily fusible tin melts and flows away from the associated alloys; then by stirring into the molten tin mats of green wood, which results in the separation of a dross carrying with it the impurities.

Properties.—Tin is a white metal and is not acted upon by air. It is a soft metal and can be readily cut with a knife; it is harder than lead, but softer than zinc. It is both ductile and malleable at ordinary temperatures and at 100° C. it can be drawn into an extremely fine wire. At a temperature just below its fusing point (232°), it becomes very brittle and may be powdered. Tin can exist in two forms, white tin, as we ordinarily know it, and a gray form. Gray tin is formed when white tin is exposed to a low degree of temperature. Below 20° C. the gray is the stable form of tin. It is reported that some of the sufferings of the Scott Exploring Expedition to the South Pole, in the last few years, was due to the crystallization (formation of gray tin) of the tin gasoline tanks. The crystalline nature of tin may be observed by etching the surface of it with dilute hydrochloric or sulphuric acids. When bent, tin emits a crackling sound, called the cry of tin, and if the bending is continued for a few times, the surface of the tin becomes heated; the heat and sound are caused by the movement of the crystalline particles. Tin boils at about 2270° ; it is a poor conductor of electricity. Hydrogen sulphide does not attack tin at ordinary temperature, consequently tinned surfaces are more permanent than silvered ones. When strongly heated, tin takes fire and burns, forming stannic oxide, SnO_2 . At red heat it decomposes steam with the formation of hydrogen. Tin forms two oxides, stannous and stannic. Stannous oxide, SnO , is prepared by treating a solution of stannous chloride with potassium carbonate, when the hydrated oxide (SnO , H_2O) is precipitated. The hydrated oxide is washed with boiling water, air being excluded, and then dried at 80° or lower. It is a black or bluish-black powder and when heated in air becomes incandescent, burning to the dioxide.

Stannic oxide, SnO_2 , exists in two forms, crystalline and

amorphous. The natural occurring tin-stone is crystalline and that prepared artificially is amorphous. The amorphous stannic oxide may be prepared by a number of methods: when tin is heated to white heat; treating stannic salts with alkali carbonates and igniting; and when tin is oxidized with nitric acid; are a few methods that may be mentioned. Stannic acid is both acid and basic in properties and forms stannic salts, exhibiting basic properties, and in stannates, its acid properties. Stannic oxide is insoluble in acids and alkalies; but is attacked when fused with potassium hydroxide, forming potassium stannate, K_2SnO_3 . Stannic oxide is used as a polishing powder and is known as "putty powder."

Tin forms two acids, stannic, H_2SnO_3 , and metastannic acid, $H_{10}Sn_5O_{16}$, or $(H_2SnO_3)_5$. The latter is formed as an insoluble powder when tin is treated with strong nitric acid. Stannous chloride, formed by dissolving tin in hydrochloric acid, is a valuable compound used in tests for certain metals and also as a reducing agent in the wet way. In an analysis of an iron ore, the iron must be in the ferrous condition; stannous chloride is the reagent used to bring about the reduction. It is also used to identify mercury in solution, reducing soluble mercuric chloride to the insoluble mercurous chloride.



Solubility.—Nitric acid attacks tin, the very dilute acid forming stannous nitrate, but the concentrated acids precipitate metastannic acid which is insoluble in acids. If alloys containing tin are "pickled" in nitric acid, that is, if the alloy be heated for the purpose of annealing and then dipped into the acid to remove oxides formed by heating, a bright metallic surface will not be produced, instead, the surface will assume a dirty appearance, due to the formation of stannic oxide. When concentrated nitric acid (sp. gr., 1.24) acts upon tin a rather violent action takes place; however, the strongest nitric acid (sp. gr., 1.5) is said to be without action upon it. Hydrochloric acid and sulphuric acid both dissolve tin and the products formed with sulphuric acid

depend upon the strength of the acid. Potassium hydroxide in the presence of air slowly attacks tin.

Uses.—Tin is used in the process of tinning, which consists of dipping sheet iron into a vessel of molten tin, thus giving the iron a superficial coating to increase the resistance of the iron to solvents and oxidation. In dentistry tin is used as tin foil in the vulcanization of rubber dentures. The tin foil is adapted to the surface of the plaster model and the denture upon removal from the flask may be separated from the tin foil either by mechanical means or by simply using a dilute solution of hydrochloric acid. The palatine portion of the upper denture, and also the portion of the lower denture covering the ridge, will be found to have a polished surface. When tin foil is not used it frequently happens that the plaster adheres very tenaciously to these portions of a denture, and any attempts to polish may ruin the piece of work. Tin foil is also used to reproduce the rugæ upon the lingual aspect of an upper denture. Again, tin foil is used as a filling material, and also with gold as a tin-gold filling. It is worked in the same manner as the so-called non-cohesive gold foils, *i. e.*, by a process of wedging. In the tin-gold fillings the tin foil is used in some cases to restore the tooth substance below the gingival margin and the filling is then finished with gold. In other cases it has been used to facilitate the introduction of gold, as in large cavities; in this instance it lessens the time it would take to introduce all gold; this saves a great amount of labor for the dentist and is not so fatiguing to the patient. Tin-and-gold fillings in some cases turn black, and resemble amalgam fillings; the theory has been advanced that galvanic action is the cause of this discoloration. In the past few years a preparation supposed to be pure tin in a shredded form was placed upon the market; this material is said to be cohesive and may be worked like cohesive gold. It was intended to be used as a filling material following the same precautions and technic as if it were gold. Because of its low conductivity of heat, non-irritating, and property of not forming compounds which would discolor tooth structures, tin has various other uses, among which might be

mentioned the following: As a non-conducting material in sensitive cavities, and in case of a perforated root, to prevent the root canal filling from being forced into the surrounding soft tissues.

Dental rubber for weighted lower dentures contains metallic tin as the weighting material. This rubber is sometimes used when there is considerable loss of tissue and the lower denture demands a very thick rubber restoration; the tin reduces the bulk of rubber and aids in the overcoming of porosity of the rubber during vulcanization. Block-tin is sometimes used in cheoplastic operations for the construction of lower dentures.

Alloys.—Tin and mercury amalgamate readily and chemical compounds having various formulas are supposed to be formed. Silver and tin form an alloy which is harder than tin. Dr. Bean's alloy, containing ninety-five parts tin and five parts silver, is used in cheoplastic operations in which the alloy is cast directly upon the vulcanite teeth.

In cheoplastic operation a wax model of the parts to be cast is made; this is invested in a suitable flask, and when the investment has hardened, the wax is removed by separating the flask and using hot water. The flask is then bolted together and the joints made tight with fresh investing materials, and the piece thoroughly dried. Molten metal is poured into the flask through the pouring gates, and upon cooling the piece is removed from the flask and receives mechanical treatment, such as filing and polishing. In some cases the metal may be poured directly against the vulcanite teeth, and the complete restoration of the lost parts made of metal, while in other cases simply a metallic base is cast and the teeth attached by the use of vulcanite rubber. Platinum and tin form an alloy which fuses at a comparatively low temperature. This alloy is hard and brittle.

Palladium also forms a brittle alloy with tin.

Lead and Tin.—These two metals readily alloy and form the so-called soft solders. The following is a list of soft solders:

	Tin.	Lead.	Bismuth.	Fusing point.
Soft, coarse	1	2	..	441° F.
Soft, fine	2	1	..	475° F.
Soft, fusible	2	1	1	

The following is a list of solders and flux used in soldering some of the metals:

Materials to be soldered.	Solder.	Flux.
Tin plate	Soft, coarse or fine	Rosin or zinc chloride.
Lead	Soft or coarse	Rosin.
Brass, copper, iron and zinc	Soft or coarse	Zinc chloride.

Tin is used as a constituent of low fusing alloys.

Dr. C. M. Richmond's alloy fuses at 150° F., and may be poured into a plaster impression without generating steam. The formula of this alloy is as follows:

Tin	20 parts by weight
Lead	19 " "
Cadmium	13 " "
Bismuth	48 " "

The following alloys may also be used:

Tin.	Lead.	Bismuth.	Melting point alloy.
1	2	2	236° F.
5	3	3	202° F.
3	5	8	197° F.

Babbitt metal, named after Isaac Babbitt, of Boston, is an alloy consisting of nine parts tin and ten parts copper, used for journal boxes. Many modifications have been made in this alloy, but the term is still applied to any white alloy employed in the construction of bearings, to distinguish it from the bronzes and brasses. Alloys used for this same purpose and known as antifriction metals, for the most part consist of lead, antimony, and tin. Dr. Fletcher recommends an alloy of copper, 4 pounds; Banca tin, 96 pounds; regulus antimony, 8 pounds. This alloy is said to be nearly as hard as zinc, while its shrinkage is much less. These qualities, together with the low temperature at which it fuses, entitle it to a place in the dental laboratory for the preparation of dies and counter-dies.

Dr. L. P. Haskell recommends the formula: tin, 72.72; copper, 9.09; antimony, 18.18.

Bronze is an alloy of copper and tin, and sometimes zinc. It is affected by changes of temperature in a manner precisely the reverse of that in which steel is affected, becoming soft and malleable when quickly cooled, and hard and brittle when allowed to cool slowly. The art of making bronze was practised before any knowledge of the working of iron existed, and it was used at a very early period in the manufacture of weapons.

Commercial tin is liable to contain minute quantities of lead, iron, copper, arsenic, antimony bismuth, etc. Pure tin may be precipitated in crystals by the feeble galvanic current excited by immersing a plate of tin in a strong solution of stannous chloride. Water is carefully poured on so as not to disturb the layer of tin solution. The pure metal will be deposited on the bar of tin at the point of junction of the water and the metallic solution.

RESUMÉ.

Symbol, Sn.	Chief ore, tin-stone, cassiterite.
Valency, II or IV.	
Atomic weight, 119.	Conductivity of heat, 145 or 6th.
Melting point, 232° C.	Conductivity of electricity, 12.22.
Specific heat, 0.0555.	Coefficient of expansion, 0.00002173.
Boiling point, 2270° C.	Ductility, 7th.
Color, white.	Tenacity, 7th.
Malleability, 3d.	
Specific gravity, 7.29.	
Crystalline form, quadratic	

CHAPTER XV.

GOLD.

Symbol, Au (aurum). Atomic weight, 197.2.

Occurrence.—Gold occurs in nature in the native state: It is found present in small quantities in certain sulphides and also in combination with tellurium.

Native gold with comparatively few exceptions is found in veins of quartz. The gold occurs in the quartz, irregularly distributed in strings, scales, plates and in masses. As the result of erosive changes occurring in the vein formation gold is also found in the gravel or sands of rivers and valleys and these are known as alluvial deposits. Gold as it occurs in vein formation is sometimes spoken of as *reef-gold*.

Alluvial gold occurs as dust, grains and larger pieces (nuggets) in alluvial deposits, which form beds of sand or gravel, either upon the surface, called shallow placers, or at greater or less depth (deep placers), which have been produced by the destruction of the gold-bearing deposits.

Gold nuggets of enormous size have been found at various times, the Australian gold region has yielded two nuggets, one weighing 184 and another 190 pounds. Eggleston states that the gravels of California have yielded a nugget weighing 2250 ounces troy (153 pounds avoirdupois).

Native gold ordinarily contains up to 16 per cent. of silver. The purest which has been described is that obtained from Mount Morgan in Queensland, which has yielded 99.7 to 99.8 per cent. of gold, the remainder being copper, iron and only a trace of silver. The native metal usually contains silver, copper, bismuth, rhodium, or palladium.

According to Wagner the following is a list of analyses of native golds obtained from various sources:

	Transyl- vania.	S. America.	Siberia.	California.	Australia.
Gold	64.77	88.04	86.5	90.60	99.20 to 95.7
Silver	35.23	11.96	13.2	10.06	0.43 to 3.8
Iron and other metals . .			0.3	0.34	0.28 to 0.2

Small quantities of native amalgam have also been found.

Sulphides Containing Gold.—Pyrite sometimes contains gold distributed invisibly through it; the ore, auriferous pyrite is an important source of gold and ranks next to the native metal as a source of gold.

Arsenopyrite is mined in Ontario for the gold which it contains.

Chalcopyrite, the chief working ore of copper, may also contain gold and silver, and special metallurgical processes must be made use of for the removal of the metals from copper.

Marcasite, galena and sphalerite also frequently contain gold.

Minerals of Gold.—The tellurides are possibly the only compounds of gold occurring in nature to any great extent. Sylvanite, $(\text{AuAg})\text{Te}_2$, contains about 24 to 26 per cent. of gold. This mineral is found in Transylvania, California and Colorado. Krennerite has the same formula as sylvanite.

Calaverite, $(\text{AuAg})\text{Te}_2$, with Au contains about 42 per cent. of gold.

Nagyagite or foliated tellurium, $(\text{Pb, Au})_2(\text{STeSb})_3$, contains only about 5 to 9 per cent. of gold. The tellurides are the principle gold-bearing ores of Colorado, and to show the importance of these ores, Colorado in 1913 produced 878,021 ounces of gold having a valuation of \$18,148,711.27.

In December, 1914, a deposit of calaverite and sylvanite was discovered in the Cresson mine located at Cripple Creek, Col., at a depth of 1265 feet. The amount of gold that the deposit will produce has not been estimated; however, it is considered the greatest strike of its kind ever made. Gold is a universally occurring element, small quantities being present in sands and also surface and sea waters; however, it is present in such small quantities that it cannot be profitably recovered. The richest sources, and the value of the

gold recovered in various localities for the year 1914, are as follows:

	Oz. fine.	Value.
Africa { Transvaal		
Cape Colony, etc. }		
United States	8,395,964	\$173,560,000
Russia	4,573,976	94,531,800
Australia	1,382,897	28,587,000
Balance of the world . .	1,232,973	25,487,800
	6,453,728	

The following represents the production in the United States for 1914 from the three principal sources:

	Oz. fine.	Value.
California	1,028,061	\$21,251,900
Colorado	962,779	19,902,400
Alaska	800,471	16,547,200

Historical.—Gold has been known and used by mankind from the earliest of times. It has been made use of for ornamental purposes and as a circulating medium, because of its scarcity, beautiful color and also its resistance to corrosive influences. Gold has played a very important part in the development of the human race, politically, and also scientifically.

The history of America shows that the finding of gold was ever before the minds of the early explorers. Columbus, in his second voyage in the year 1493, found Jamaica and the other islands, and sought for gold but was not successful. Cortez in his search for gold was led to Mexico and his exploits to obtain this metal is a good illustration of the influence gold has had upon mankind. About \$17,500,000 worth of gold was a little later seized by the Spaniards from the Incas in Peru. De Sota and De Coronado, both in search of gold, were led to regions unexplored. These few illustrations show how the search for gold caused the exploration of the various parts of the western hemisphere; in fact, as soon as a new territory had been discovered in the past, one of the first inducements to settlers was the thought of the discovery of gold. The famous gold fever of "49", causing trains of prospectors to cross the prairies and the intense hardships endured in their attempt to reach California

and her gold fields, and later the rush to Alaska, tends to show how this metal has caused new districts to be peopled and also its influences upon humanity.

It has caused the conquest of nations, the enlargement of dominions, the development of industry in all its branches, and on the other hand, every crime conceivable has been committed for its possession.

The search for gold has led to the development of the various sciences. In the olden times great efforts were expended by the alchemists to find a simple method of producing the metal, thus causing the development of chemistry and its allied sciences. At the present time it is one of the prime objects of the metallurgical world to produce this metal at the least possible expense. The effect is that metallurgy has received one of its principal stimuli from gold.

The Extraction of Gold.—Gold is obtained from its ores by metallurgical processes or by direct washing.

Direct Washing Process.—There are three methods of direct washing: (1) Placer mining. (2) Hydraulic mining. (3) Dredging.

Placer Mining.—Placer mining is at the present time rarely used because of the heavy loss of gold entailed by its use; this may amount to 50 per cent. of gold present in the pay dirt. At one time the prospectors used the so-called *pan*. In panning, a black sheet-iron, sheet-tin or wooden pan, about 16 inches in diameter and 2 inches deep, was used. The pan was filled about two-thirds full of pay dirt and then held in a stream or pool of water. The pan was given a twisting motion and the heavier particles of gold descended to the bottom of the pan. The cradle and the Long Tom are other devices for carrying on this same process on a larger scale. At the present time they are used to some extent by the Chinese of California, in washing tailings which have already been washed several times. With the cradle a man may wash $1\frac{1}{2}$ cubic yards of gold-bearing sand in a day, while with the Long Tom two men can wash about 8 cubic yards. The loss of gold by these methods is also very heavy.

The *sluice* is the appliance mostly used in the United States in the washing process. It consists of a series of troughs or boxes, about 1 foot 4 inches wide and 9 inches deep. Each box is 12 feet long and is so connected as to form long troughs, inclined about 8 to 20 inches to each 12-foot box. They are fitted with wooden slats or riffles, which are wedged into place, either longitudinally or transversely, to assist in the breaking up of the earthy matter. At certain points under currents are placed to separate the coarser pebbles. These are formed by replacing the bottom of a sluice by a grating known as a *grizzly* and leaving the end of the box open. Underneath the grating there is a trough at right angles to the main, leading to other sluices parallel to the first. The finer and heavier gold-laden material passes through the grating and is carried to the second line of sluices which are much wider and not so deep; this gives the gold an opportunity to settle in the sluices. Mercury is generally sprinkled into the cross riffles and amalgamates with the gold.

Hydraulic Method.—Water is forced into the gold-bearing gravels under high pressure and then conveys the gravel into long sluices. The gold is taken up by mercury, and the amalgam submitted to dry methods of refining.

Dredging.—Dredging the river beds for gold has attracted some attention within recent years. Some of the dredge buckets used have a capacity of 16 cubic feet and dredge and wash 300,000 cubic yards at a cost of less than three cents a cubic yard. The drawback to this industry is the high cost of electricity. Fig. 48 illustrates a dredge in use in one of the districts of Colorado.

Quartz and also telluride mining is the same as any other form of vein mining. Fig. 49 illustrates a typical underground scene. Precautions are taken at the present time to prevent accidents of all types characteristic of this form of labor. The laws require the mine to be timbered so as to prevent caving in; several ways of egress are also constructed; the drip water is drained and also by properly placed fans the air is kept in constant circulation. The ore is blasted

from place and then carried to the surface. It is then dressed and concentrated and sent to the smelters or refineries.

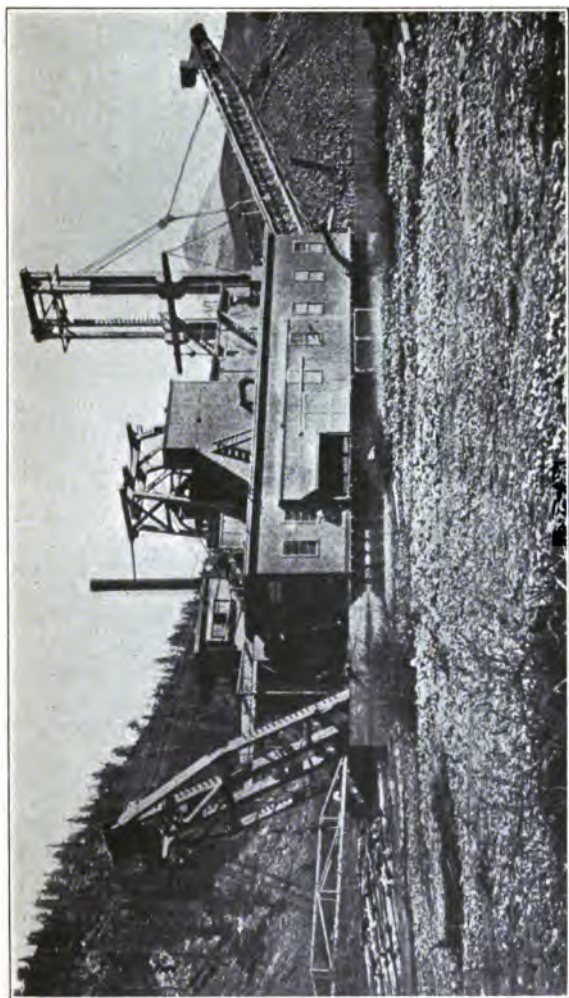


FIG. 48

Recovery of Gold from its Ores.—The methods of recovery of gold from its ores may be classed as follows:



FIG. 49

1. Extraction by simply washing.
2. Extraction in the dry way.
3. Extraction in the wet way.
4. Extraction by electrolysis.
5. Extraction by wet and dry methods.

SIMPLE WASHING.—Extraction by simply washing is effected by dressing gold-bearing sands, gravels, or ores.

DRY METHOD.—Extraction in the dry way consists of converting the gold into gold-lead, or gold-lead-silver alloy and cupelling it. This method is used in extracting gold, when present in small but paying quantities in other ores, such as iron-lead and gold-bearing furnace products from other metallurgical reductions.

WET METHODS.—Under this heading there are three distinct processes: (1) Amalgamation process. (2) Chlorination process. (3) Cyanide process.

Amalgamation Process.—The gold ore is treated with mercury and an amalgam of gold and mercury is formed. The amalgam usually contains silver, but is free from contamination of base metals. The mercury is boiled off, leaving a gold-silver alloy. A special process is necessary to free the gold from silver.

Chlorination Process (Plattner or Percy Process).—This process consists of treating gold ores with watery solutions of chlorine. It is used to treat ores in which mercury has failed to recover all the gold present. The gold is dissolved as the chloride and is then precipitated from solution by the addition of ferrous sulphate:



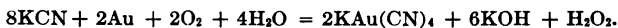
In the Plattner process the following operations have to be considered:

1. Clacination of the ore.
2. Chlorinating the gold and leaching the auric chloride from the ore.
3. Extraction of the gold from the solution of its chloride.

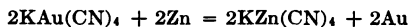
If the gold ore contains silver, the silver chloride, being insoluble in chlorine, remains in the residues. In this case,

after the gold has been removed, the residues are treated with hyposulphides to recover the silver.

Cyanide Process.—Potassium cyanide in the presence of air possesses the property of dissolving gold according to the following reaction:



From this solution gold may be recovered either by heating with zinc shavings:



or by electrolysis, using a cyanide bath.

Reduction of Tellurides.—The process made use of in the reduction of tellurides consists of dressing and roasting the ore and submitting the mass to an amalgamation and cyanide recovery process. A description of this process will give a knowledge of the actual working of a gold ore. The ore is passed through a ball mill and crushed; it is then conveyed to mixing bins so as to obtain a uniform product. Belt conveyors are then used to transfer the ore again to the ball mills and it is further ground, until it will pass through a screen one-eighth inch square. The ore is next sent to the roasters and the tellurium burned out first and then the sulphur, leaving about 0.07 per cent. of sulphur still in the ore. The temperature of the roasting furnace ranges from 700° to 1300° F. After cooling the mass the ore is sent to the cyanide tanks and thoroughly mixed. The mass is again ground until it passes through a screen $\frac{1}{16}$ of an inch square. This product is then allowed to flow over blanket tables, upon which the coarse particles of gold produced in the roasting process is recovered and subsequently reduced to amalgam form by pan amalgamation. The cyanide solution is obtained from the sands and then reduced by zinc shavings. The gold-zinc product is placed in suitable vessels and the zinc dissolved and washed away. The amalgam is heated and the mercury driven off and the gold recovered.

ELECTROLYTIC PROCESS.—This process is used for the most part in the treatment of gold-copper and gold-silver alloys and also as a “parting process.”

Refining Gold.—Gold as it is obtained from the processes mentioned contains impurities. The greater part of silver produced contains gold as also does the greater part of the gold contain silver. These silver-gold and gold-silver alloys may also contain such metals as lead, bismuth, tin, antimony and arsenic, which must be removed as far as possible before parting by means of cupellation or refining. The process of parting has for its object the removal of the last traces of foreign elements in addition to separating silver from gold. Parting may be accomplished either in the dry or wet way or electrolytically. The dry way depends upon the conversion of the silver into sulphide or chloride, while gold is not acted upon by either chlorine or sulphur at high temperatures. Briefly described, the following methods are made use of in the dry way:

1. The gold-silver alloy is melted with antimony sulphide, the silver combines with the sulphur and an alloy of antimony and gold results. By heating the alloy, antimony is volatilized, leaving the gold.
2. Parting by means of sulphur and litharge.
3. Parting by sulphur alone.
4. Parting by means of pyrites.
5. Parting by means of salt or cementation.
6. Parting by chlorine gas.

Most of these processes are obsolete; however, the last one is used at the present time to some extent.

The alloy is fused in a glazed clay crucible and a covering of borax is used, chlorine gas is forced through the molten alloy and silver chloride separates from the gold.

WET METHOD OF PARTING.—The wet method of parting is generally known as the inquartation process, because the gold-silver alloy is so prepared that it contains three parts of silver to one part of gold, making up a four-part alloy; from this we have the derivation of the name quartation, from quarter, meaning four.

If the gold contains tin, antimony or arsenic, it should be refined by fusion before this process is used. Palladium, copper and lead may be present in the alloy without inter-

fering with this process. The alloy is prepared by adding a sufficient quantity of silver to approximately produce a 1-to-3 alloy of gold and silver. The mass is granulated by pouring the fused alloy into water contained in a wooden vessel; a second granulation is desirable, as it produces a more homogeneous alloy. The next step is to treat the alloy with either nitric acid (sp. gr., 1.4), or sulphuric acid (sp. gr., 1.84).

Nitric Acid Method.—The granulated alloy is placed in a porcelain or glazed earthenware pot and treated with about 90 per cent. by weight of nitric acid (sp. gr., 1.4). Heat is applied and the granulations are stirred every twenty minutes to prevent them from clotting together. After boiling for twelve hours and settling for twelve, the silver nitrate solution is diluted with water and drawn off. The residue is again treated with nitric acid as before for twelve hours and allowed to settle for the same period of time. The gold is filtered off and washed with boiling water and then boiled with sulphuric acid three times. The gold from this process may be obtained 999.5 fine.

Sulphuric Acid Process.—This process is more extensively used than the nitric acid process. The following operations are embraced in this procedure:

1. The preparation of an alloy suitable for parting and its granulation.
2. The solution of the silver of the alloy by means of sulphuric acid.
3. Obtaining the gold from the auriferous residue.

Lead, bismuth, tin, antimony, arsenic and tellurium seriously interfere with the malleability of gold and should be removed before the gold-silver alloy is prepared. From argentiferous gold these metals may be removed by fusing with potassium nitrate. Copper during this process forms an insoluble anhydrous copper sulphate which clings to the granulated metal and prevents the action of the acid. When copper is present in an appreciable amount the proportions of gold to silver should not exceed about 10 per cent. The alloy is prepared in other cases containing two parts of gold

to four of silver and the copper should not exceed 6 per cent. The granulated alloy is treated with sulphuric acid (specific gravity, 1.84), in three successive stages; it is then thoroughly washed, dried, pressed and finally melted. Its fineness is from 990 to 994 parts per thousand. To prepare gold of a higher standard than that produced from these processes, the following methods are made use of:

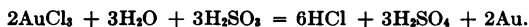
The purest gold, completely free from silver is obtained by Roessler's method. The gold from the sulphuric acid parting is treated with aqua regia in a porcelain vessel. It is then precipitated by means of ferrous sulphate. The gold thus obtained is from 999.4 to 999.9 parts per thousand fine. By passing chlorine gas through molten gold a product 997 fine can be obtained.

Treatment of Gold Scraps in the Dry Way.—The following agents may be used to remove impurities from gold scraps in the dry way, and brittleness in a great measure may be overcome; it stands to reason that if the gold is desired in a high degree of purity, the chlorine process or aqua regia methods should be used.

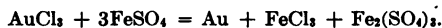
Potassium nitrate oxidizes certain base metals; however, this reagent attacks graphite crucibles, and borax which is used as a flux will attack fire-clay crucibles. Lead is hard to remove by potassium nitrate alone; however, when used in conjunction with ammonium chloride most of the lead will be oxidized and taken up by the borax. Sand may be used when iron is present, while potassium carbonate removes tin. The following is a brief outline of a method used to overcome brittleness: Fuse the gold, using borax as a flux then add ammonium chloride to remove lead and tin. Remove the slag and place a small quantity of mercuric chloride upon the surface of the molten metal; this will volatilize zinc, copper, antimony and bismuth as chlorides. The metal is then covered with powdered charcoal, stirred and poured.

Agents Used to Precipitate Gold from Solution.—*Sulphurous acid*, H_2SO_3 , precipitates gold generally in the form of a scaly metallic powder; hence it does not afford masses sufficiently

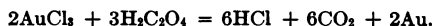
coherent or sponge-like for use as a filling material for the dentist. The reaction which takes place is thus explained:



Ferrous sulphate, FeSO_4 , precipitates gold in the form of a light brown powder. About four times the weight of gold is the quantity of ferrous sulphate required to completely precipitate all of the gold from solution. After the finely divided gold has entirely subsided, it should be boiled several times with dilute hydrochloric acid to entirely remove all traces of iron. If there is a possibility of platinum being present, it should be precipitated first, as ferrous sulphate also throws this metal out of solution. The reaction of ferrous sulphate on gold chloride is represented by the following:

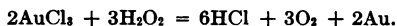


Oxalic Acid, $\text{H}_2\text{C}_2\text{O}_4$.—This organic acid is the best reagent for the precipitation of gold; however, it is somewhat slower in its action than the other precipitants. The gold is thrown down by oxalic acid in various forms, from sponge-like masses to the different crystalline or powdery forms. Heat is necessary and also causes the more rapid precipitation. The reaction is shown in the following equation:



Gum arabic may also be used and it precipitates gold in the shredded form.

Sugar, hydrogen peroxide, and certain metals among which may be mentioned lead, silver, mercury, tin, copper, platinum and zinc also precipitates gold from its solutions. The reaction with hydrogen peroxide is as follows:



Properties.—Gold possesses a beautiful yellow color, and a brilliant metallic luster which is unacted upon by air or hydrogen sulphide. It is of about the same hardness as lead.

Gold is one of the most malleable of metals and has been beaten into leaves about $\frac{1}{367650}$ of an inch in thickness;

one grain of gold covering 75 square inches. Gold is generally considered the most malleable of metals, and as has been elsewhere stated in this text, these figures must not be taken too seriously, as our methods have failed before the limits of malleability have been reached. In comparison with the above figures 1 grain of silver has been beaten out to cover 98 square inches; although the silver is of less specific gravity, and 1 grain would necessarily mean a larger volume of this metal, but per weight silver appears more malleable than gold. To appreciate how thin a piece of metal $\frac{1}{387650}$ of an inch would be, it will take 1200 leaves of gold of this thickness to equal the thickness of a piece of ordinary writing paper.

Gold is exceedingly ductile, but does not possess a very considerable degree of tenacity. A grain of gold, however, if covered with a more tenacious metal, such as silver, may be drawn into a wire 500 feet in length, having a diameter of $\frac{1}{5000}$ of an inch.

The specific gravity of gold varies according to conditions. In the finely divided state, as it is obtained by precipitating with oxalic acid, it is 19.35. Cast gold is somewhat higher and when hammered or pressed in a rolling-mill, it may be raised to from 19.37 to 19.5. Annealing restores its original density. Gold as a conductor of electricity as compared with silver is 66.7; silver being 100. As a conductor of heat 532, silver being 1000. Its coefficient of linear expansion between 0° and 100° is 0.00001466. The boiling point of gold according to Greenwood is given as 2200° C.; however, gold containing other metals such as zinc, silver, copper, etc., may be volatilized at a temperature near the fusing point, or about 1120° C. Makins has succeeded in volatilizing it by passing a powerful charge of electricity through a highly attenuated gold wire or leaf.

Gold Leaf and Foil.—Gold foils may be obtained in various colors, depending upon the alloy of gold used. The color of the gold is modified by the admixture of silver, producing light golds, and by the alloying with copper, red or dark shades may be produced. The following colors may be produced: red, pale red, extra deep red, deep red, orange,

lemon, deep pale, pale, pale-pale, deep party, party and fine gold. The deeper colors are alloyed with from 12 to 16 grains of copper per ounce; and the middle colors, 12 to 20 grains of silver and 6 to 8 grains of copper to the ounce; the paler golds contain from 2 to 20 dwt. of silver to the ounce.

When silver and copper are used together, it is found that the gold becomes brittle and cannot be reduced to the same degree as when these metals are used separately.

For filling teeth nearly pure gold in the form of foil is used. It is generally prepared by beating, but some of the heavier numbers are produced by rolling. Foil gold is put upon the market in books containing 60 grains, the number of the foil represents the number of grains to the sheet; a book of No. 2 foil contains 30 sheets, each weighing 2 grains, consequently, a book of No. 4 foil contains 15 sheets of 4 grains each; No. 60 foil, each sheet weighs 60 grains and only one sheet to the book.

There are two varieties of foils, *cohesive* and *non-cohesive*. Cohesive foil (hard gold). Gold in a high degree of purity is all cohesive, *i. e.*, welds in the cold. This form of gold is called hard gold because upon working it, it loses its pliability and must be annealed in order to have its original softness restored. Non-cohesive (soft gold). It is the common belief that the property of non-cohesiveness is imparted to gold by some treatment of the surface or to the mechanical management during lamination, and not to alloying. Certain gases when passed over the surface of gold cause it to lose its cohesiveness.

Corrugated Gold.—Corrugated gold is prepared by placing sheets of metal between leaves of unsized paper and tightly packing in an iron box, it is then exposed to a temperature sufficient to carbonize the paper. When cool the gold is found to be non-cohesive, exceedingly soft and presents a peculiar corrugated condition of its surface. Annealing does not render it cohesive.

The process of beating gold is conducted in the following manner: The metal is first alloyed according to the color desired, and in order to improve its malleability it is melted at a higher temperature than is necessary for mere fusion.

It is then cast into an ingot and rolled into a ribbon of one-half inch in width and ten feet in length to the ounce. After this it is annealed and cut into pieces of about six and one-half grains each and placed between the leaves of a "cutch," which is about half an inch thick and three and one-half inches square, containing about one hundred and eighty leaves of tough paper manufactured in France. Fine vellum was formerly used for this purpose, and it is yet often interleaved in the proportion of about one vellum to six of paper. The hammer employed by gold-beaters weighs about seventeen pounds, and rebounds, by the elasticity of the skin, to such an extent that each stroke involves but little labor. It requires about twenty minutes' beating to spread the gold to the size of the cutch, and if it is intended for filling teeth it is carried no further than the cutch stage. If, however, it is to be still further attenuated, each leaf is taken from the cutch and cut into four pieces, when it is put between the skins of a "shoder," four and one-half inches square and three-quarters of an inch thick, containing about 720 skins. The shoder requires about two hours' beating with a nine-pound hammer. As the gold will spread unequally, the shoder is beaten upon after the large leaves have reached the edges, the effect of which is that the margins of large leaves come out of the edges in a state of dust. This allows time for the smaller leaves to reach the full size of the shoder, by which a general evenness in the size of the leaves is obtained. Each leaf is again cut into four pieces and placed between the leaves of a "mold"—an appliance composed of about nine hundred and fifty of the finest gold-beater's skins. Its dimensions are five inches square by three-fourths of an inch thick. The management of the gold in the "molds" is the last and most difficult stage in the process of gold-beating, and the fineness of the skin and judgment of the workman will greatly influence the final result.

The process of lamination may be thus described: During the first hour the blows of the hammer are directed principally upon the center of the mold, by which means the edges of the leaves are made to crack, but they soon coalesce and

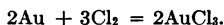
unite, so that after beating no trace of the rupture is left. After having been beaten for an hour in a mold until the leaves have attained a thickness of $\frac{1}{150000}$ part of an inch in thickness, green rays of light begin to be transmitted, if the gold is pure; but if largely alloyed with silver, rays of a pale violet hue pass through the gold.

The membrane called "gold-beater's skin," used in the make-up of the shoder and mold, is the outer coat of the cecum or blind gut of the ox. It is immersed in a potash solution and scraped with a blunt knife to free it from fat. It is then stretched on a frame, two membranes are glued together, treated with camphor in isinglass and subsequently coated with albumen, and cut into squares of five or five and one-half inches, and is ready for use. It is stated that the ceca of 380 oxen are required to yield enough of the membrane to make up one mold of 950 pieces, only two and one-half skins being obtained from each animal. Dryness is a matter of great importance and, as the leaves are liable to absorb moisture from the atmosphere, they require hot pressing every time they are used, and if this precaution is neglected the leaf will be pierced with innumerable holes or reduced to a pulverulent state.

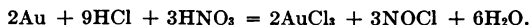
Solubilities.—The ordinary acids are without action upon gold, selenic acid, H_2SeO_4 , is said to dissolve it and the other noble metals. Chlorine, bromine, and iodine dissolve gold with the formation of the corresponding salts. Aqua regia is the best solvent for gold and its action is dependent upon the liberation of chlorine from the hydrochloric acid by the oxidizing power of nitric acid. The chlorine attacks the gold with the formation of the trichloride; writing this reaction in two stages, we have the following:



Chlorine is given off and also nitrosyl chloride (NOCl).



The complete reaction may be represented as follows:



Potassium cyanide in the presence of air dissolves gold, with the formation of potassium auric cyanide. In metallurgical operations the cyanide solution used is of about 0.25 per cent. strength.

Alloys.—Gold readily amalgamates with mercury in all proportions and the amalgam is soluble in mercury. Amalgam containing 90 per cent. of mercury is fluid, with 87.5 per cent. it is pasty, and with 87 per cent. it forms yellowish-white crystals. Solutions of the amalgam in mercury, when pressed through chamois leather, leaves a residue containing 66 per cent. of gold and the mercury which passes through the leather bears a little gold, the amount depending upon the temperature.

Several compounds are said to be formed corresponding to the formulas:



The presence of lead, bismuth, cadmium, antimony, arsenic and tin, render gold brittle even when present in small quantities; $\frac{1}{2000}$ part of lead, bismuth or tin produces brittleness in gold. Zinc also renders gold brittle but in the presence of copper and silver does not materially affect the malleability. Osmium and iridium do not alloy with gold but remain as grains in the molten mass.

Silver and gold alloy in all proportions and the color of the gold is lightened by the addition of silver. Molten gold-silver alloys containing less than 20 per cent. of gold deposit; when slowly cooled an alloy containing one part of gold and five parts of silver and the mother liquid contains but little gold. Fenchel states that the fusing point of gold is hardly lowered by the addition of silver even to the extent of 50 per cent.; an alloy of sixty parts silver and forty parts gold requires more than 1050° C. to melt. Prothero calls attention to this same fact and states that the difference in the fusing point of a 50 per cent. silver alloy and that of pure gold could not be registered with a pyrometer. However, both of these authorities disagree as to the usefulness of silver in

gold alloys. Copper and gold form a durable alloy, but in order to obtain a uniform product the alloy should be heated for some time. The malleability of the gold is not, however, much effected by admixtures with copper. Tin when alloyed to gold decreases the melting point; an alloy containing about 37 per cent. tin and 63 per cent. gold fuses at 418° C. This alloy is as brittle as glass but withstands the action of acids. Antimony with gold produces brittle alloys which are very hard and low fusing. Gold and iridium form very hard alloys, and the presence of iridium in gold bullion has caused a great amount of trouble, as such gold is extremely hard and interferes with the operations made use of in the processes of coinage. Iron and gold alloy and the alloy resembles iron in color, when the percentage of gold does not exceed 80 per cent. These alloys are said to be brittle and very hard to work. They have no useful application. Care should be taken not to contaminate gold with iron, as the working properties will be interfered with. It is rather easy to contaminate gold with iron in the dental laboratory and if the precaution be taken to use a magnet upon the gold scraps this difficulty will be overcome. In teasing solder it is the best practice to use a slate instrument rather than an iron instrument for the same reason.

Platinum and gold alloy, producing an alloy which adds somewhat to the elasticity of the gold. An excess of platinum renders the alloy infusible in the ordinary blast furnaces.

This alloy is used as a clasp metal in dentistry. Prothero claims that a 10 per cent. copper-gold alloy possesses the same hardness as a 25 per cent. platinum-gold alloy.

Platinum and gold in the form of foil is also used under the name platinized gold, for filling cavities, where gold has proved too soft. Platinized gold may be prepared by electro-depositing a gold surface upon platinum.

Palladium and gold readily alloy and the hardness of gold is increased. There is a difference of opinion whether palladium renders gold brittle or not; Makins claims that the least trace of palladium renders gold brittle; however, later experiments seem to show that in reasonable quantities

palladium does not affect the malleability and ductility of gold to any appreciable extent.

Gold and zinc combine, forming very brittle alloys, and the fusing point of the gold is considerably reduced. Zinc is sometimes added to gold-copper alloys because of the reducing powders of zinc. The zinc is supposed to take up the oxygen and thus prevent loss of copper during the fusing process.

Certain alloys of gold are used in dentistry for the construction of metallic bases, and also as a solder.

Gold alloys used in dentistry should be considered as to the character of the metals made use of.

The requirements that such an alloy should possess are generally classed under the following headings:

1. The color of the alloy should not be objectionable.
2. It should not be acted upon by the fluids of the mouth.

These requirements are looked to, no matter to what purpose the alloy is put. Little need be said in regard to the first requirement, for the color of any of the metals may be said to be objectionable at the best.

A metallic body in the mouth may be acted upon by direct chemical processes; hydrogen sulphide causes a discoloration in some alloys; fruit acids also may attack some metallic substances. Metals may also be attacked by reason of a difference in their electropotential, that is depending upon their position in the electromotive series; a voltaic couple may be produced, one of the metals being electropositive to the other and the saliva having salts in solution, there is then present all the elements of a so-called voltaic cell. Dr. C. J. Grieves has written a very interesting article upon the "Behavior of Certain Metals in the Mouth." Quoting from this article: "An alloy containing approximately gold 18, platinum 2, the remaining 2 parts being made up of equal parts silver, copper and zinc, after short wear under like conditions presents corrosion almost as pronounced as German silver." "The study of a large number of 18-carat gold solder surfaces known to have been smooth when placed in the mouth, develops the interesting fact that whenever

a food-retention center was created, corrosion exists to a marked degree."

Considering the first alloy mentioned, gold, platinum, silver and copper are classed as negative metals, while zinc is strongly electropositive; the greatest potential difference exists between gold and zinc, and from this point of view the alloy would be more resistant to the action of the saliva, if zinc would have been eliminated. The same may be said of the 18-carat solders containing zinc. Working upon this principle, an alloy to possess the greatest resistance to the fluids of the mouth should contain only those metals from hydrogen to gold (see electromotive series).

Gold is Alloyed for Dental Purposes.—1. To increase its hardness.

2. To lower its fusing point, as in the construction of solders.

3. To increase its elasticity, as in the construction of clasp metal.

Depending upon the quantity of gold present in an alloy, pure gold is taken as a standard and called 24-carat; the degree of fineness is expressed on a basis of twenty-four parts.

The carat is the term used to express the purity of gold and represents one-twenty-fourth parts.

Plate gold is generally expressed in caratage; that is, 22-carat plate gold contains twenty-two parts of pure gold and two parts of the metals.

Solder is expressed in caratage of the gold for which it is intended to be used upon as a solder. For example, 18-carat gold solder is not 18 carats fine, but is supposed to be used as a solder for 18-carat, or better, plate gold. Eighteen-carat solder generally is about 16 carats fine.

The hardness of gold is increased in order for the gold to withstand the form of attrition to which it is subjected during the process of mastication.

Copper is a very serviceable metal for this purpose; however, it reduces the fusing point of gold. The alloy is of a dark red color, and copper is also liable to oxidation on

overheating. There is very little electropotential difference between copper and gold. These metals should be alloyed and kept in the molten condition for some time, so as to obtain a homogeneous mixture; the surface of the molten metals also should be protected to prevent loss by oxidation while alloying. The United States gold coin contains copper to harden the gold; it is made up of gold ninety parts and copper ten, or about 21.6 carats fine.

Silver hardens gold and tends to lighten its color; in larger proportions an alloy results having a brassy appearance. The fusing point of the alloy is scarcely altered. In alloying, the metals must be kept in the state of fusion for some time, in order to obtain a uniform mixture.

To Lower the Fusing Point of Gold.—Zinc and copper have been the principal metals used in dental gold, which reduced the fusing point to the extent that was necessary for soldering purposes. Dr. Dorrance prepares an alloy consisting of:

Pure silver	1 pennyweight
Pure zinc	2 pennyweights
Pure copper	3 pennyweights

To prepare a solder for a given carat gold, a piece of the plate gold is alloyed with a given quantity of this alloy; for example, if 22-carat plate is to be soldered, then 22 grains of the plate is alloyed with 2 grains of the Dorrance alloy.

Gold plate suitable for dental purposes may be prepared according to the following formulas, from Richardson's *Mechanical Dentistry*:

GOLD PLATE 18 CARATS FINE.

No. 1.		No. 2.	
Pure gold .	18 pennyweights	Gold coin .	20 pennyweights
Pure copper .	4 pennyweights	Pure copper .	2 pennyweights
Pure silver .	2 pennyweights	Pure silver .	2 pennyweights

GOLD PLATE 19 CARATS FINE.

No. 3.		No. 4.	
Pure gold .	19 pennyweights	Gold coin .	20 pennyweights
Pure copper .	3 pennyweights	Pure copper .	25 grains
Pure silver .	2 pennyweights	Pure silver .	40 + grains

GOLD PLATE 20 CARATS FINE.

No. 5.		No. 6.	
Pure gold	20 pennyweights	Pure gold	20 pennyweights
Pure copper	2 pennyweights	Pure copper	18 grains
Pure silver	2 pennyweights	Pure silver	20 + grains

GOLD PLATE 21 CARATS FINE

No. 7.		No. 8.	
Pure gold	21 pennyweights	Gold coin	20 pennyweights
Pure copper	2 pennyweights	Pure silver	3 + grains
Pure silver	1 pennyweight		

No. 9.

Gold coin	22 pennyweights
Pure copper	6 grains
Pure platinum	7½ grains

GOLD PLATE 22 CARATS FINE.

No. 10.

Pure gold	22 pennyweights
Fine copper	1 pennyweight
Pure silver	18 grains
Pure platinum	6 grains

GOLD PLATE 18 CARATS FINE.

No. 11.

United States gold coin (\$60)	64½ pennyweights
Pure silver	13 pennyweights

On account of its greater strength and the power of resisting chemical action of the fluids of the mouth, many dentists prefer to use gold plate of 20 or 21 carats fine, in which the resulting constituents are copper and platinum, the following formula being an example:

Gold coin	20 pennyweights
Pure platinum	10 grains

The following formulas will produce alloys of 20 carats fineness, suitable for clasps, backings, etc., wherever elasticity and additional strength are required:

FORMULA No. 1.

Pure gold	20 pennyweights
Pure copper	2 pennyweights
Pure silver	1 pennyweight
Pure platinum	1 pennyweight

FORMULA No. 2.

Coin gold	20 pennyweights
Pure copper	8 grains
Pure silver	10 grains
Pure platinum	10 grains

Alloys of Gold Employed in Dentistry as Solders.—These are a class of alloys formed of the metal to be united, the fusing point of which is reduced by the addition of silver or copper.

14 CARATS FINE.

American gold coin . . .	\$10.00
Pure silver	4 dwts.
Pure copper	2 dwts.

16 CARATS FINE.

Pure gold	11 dwts.
Pure silver	3 dwts., 6 grs.
Pure copper	2 dwts., 6 grs.

18 CARATS FINE.

Gold coin	30 parts
Pure silver	4 parts
Pure copper	1 part
Brass	1 part

20 CARATS FINE, FOR CROWN AND BRIDGE-WORK.

American gold coin (21.6 carats fine)	
\$10 piece	258 grs.
Spelter solder	20.64 grs.

20 CARATS FINE.

Pure gold	5 pennyweights
Pure copper	6 grains
Pure silver	12 grains
Spelter solder	6 grains

20 CARATS FINE, FOR CROWN AND BRIDGE-WORK.

Zinc	1½ grains
Pure gold	20 grains
Silver solder	3 grains

Dr. C. M. Richmond's solder for bridge-work:

Gold coin	5 pennyweights
Fine brass wire	1 pennyweight

Dr. Low's formula for solder in crown and bridge-work:

19 CARATS FINE.

Coin gold	1 pennyweight
Copper	2 grains
Silver	4 grains

Spelter solder, composed of equal parts of copper and zinc, is sometimes employed as a constituent in the preparation of gold solders for the purpose of reducing the fusing point. Thus some dentists use an alloy composed of:

18-carat gold	6 pennyweights
Granulated spelter solder	6 grains

An alloy of this composition is exceedingly brittle, and hence difficult to roll into plate without breaking into many pieces. Its color is good, but the surface of such solders, after flowing, is apt to be pitted with small holes, and has

not the solid and uniform appearance that is desirable. This may be due to the oxidation and escape of some of the zinc.

The following gold alloys for dental purposes have been recommended by Dr. Prothero:

	Gold.	Plati- num.	Pallad- ium.	Silver.	Copper.	Carat.	Fusing point.
Gold plate No. 1 .	88.0	7.5	2.5	2.0	...	21.1	2075° F.
Gold plate No. 2 .	84.5	8.5	2.0	0.5	4.5	20.18	1975° F.
Casting gold "B" .	80.0	9.5	2.5	1.0	7.0	19.2	1900° F.
Casting gold "C" .	80.5	6.5	2.0	2.0	9.0	17.7	1800° F.

Methods of Reducing Gold to a Lower or Higher Standard of Fineness, and of Determining the Carat of any Given Alloy.—

In mintage the proportion of gold in an alloy is expressed in one-thousandths, but in the jewelry trade the term carat is used to designate the proportion, and it is equal to one-twenty-fourth. For instance, 6-carat gold means that of twenty-four parts of a given alloy, six parts are gold. The gold alloys used in the laboratory are generally made from pure gold or gold coin, the standards of which are definitely fixed. A few simple rules are here given,¹ by which the operator may readily determine the quantity of alloy necessary to reduce either coin or pure gold to any desired standard. To ascertain the carat of any given alloy, multiply 24 by the weight of gold in the alloyed mass and divide the product by the weight of the mass. The quotient is the carat sought. For example, take the following:

Pure gold	18 parts
Copper	4 parts
Silver	2 parts
	<hr/>
	24 parts

The result may be thus expressed:

$$24 \times 18 \div 24 = 18 \text{ carats.}$$

To reduce gold to a required carat, multiply the weight of gold used by 24 and divide the product by the required carat. The quotient is the weight of the mass when reduced,

¹ Richardson's Mechanical Dentistry.

from which subtract the weight of the gold used, and the remainder is the weight of the alloy to be added.

To raise gold from a lower to a higher carat, multiply the weight of the alloyed gold used by the number representing the proportion of alloy in the given carat; divide the product by the figures representing the quantity of alloy in the required carat. The quotient is the weight of the mass when reduced to the required carat by adding fine gold. Thus, to raise 1 pennyweight of 16-carat gold to 18 carats, the numbers representing the proportions of alloys are obtained by subtracting 18 and 16 from 24. The statement is:

$$6:8::1:1\frac{1}{2};$$

from which it will be seen that to raise 1 pennyweight of 16-carat gold to 18 carats, one-third of a pennyweight of pure gold must be added to it.

Again, if instead of using pure gold we desire to raise the fineness of 1 pennyweight of 16-carat gold to that of 18, by the addition of, say, 22-carat gold, the numbers representing the proportions of the alloy would be found by subtracting, in the example given, 16 and 18 from 22, the result being:

$$4:6::1:1\frac{1}{2}.$$

Hence, each pennyweight of 16-carat gold would require a half-pennyweight of 22-carat gold to raise it to 18 carats. The former is the system employed at the United States Mint and by metallurgists and chemists, while the latter is the usual method of expressing the grade of alloys of gold among dentists and jewelers. The following table will show the relation of one to the other:

	Carats.	Decimals.
Pure gold	24.0	1000.0
English coin	22.0	916.6
American coin	21.6	900.0
Dentists' gold	20.0	833.3
Dentists' gold	19.2	800.0
Jewellers' gold, best	18.0	750.0
Jewellers' gold, good	15.0	625.0
Jewellers' gold, low grade	12.0	500.0
Common jewellers' solder	8.0	333.3

Purple of Cassius.—Purple of Cassius is the material used to impart the color to a porcelain body, imitating the color of the soft tissues of the mouth. It is named after the discoverer, M. Cassius, who first employed this material for the above purpose. It may be prepared in the wet way by adding stannous chloride containing a little stannic chloride to the chloride of gold. A purple precipitate is formed, the composition of which is not definitely known. However, it is supposed by some to be stannous stannic oxide, aurous and auric oxide. As prepared in this manner "Oswald" claims the precipitate to be colloidal gold in stannic acid. The following methods may be used when a quantity of this material is desired: Seven parts of gold are dissolved in aqua regia and mixed with two parts of tin, also dissolved in aqua regia. This solution is largely diluted with water, and a weak solution of one part of tin in hydrochloric acid is added, drop by drop, until a fine purple color is produced. The purple of Cassius, in a state of fine division, remains for a time suspended in the water, but finally subsides as a purple powder. The fresh precipitate dissolves in ammonia, and exposure to light decomposes the purple solution, during which process its hue changes to blue, and it finally becomes colorless, and metallic gold is precipitated, the bin oxide of tin being left in solution.

The Dry Method.—The dry method is the one mostly employed now in the manufacture of this article. Professor Wildman is the authority for the following procedure: 240 grains of pure silver, 24 grains of pure gold, and $17\frac{1}{2}$ grains of pure tin are placed in a crucible, with sufficient borax to cover the mass, and melted. In order to ensure a thorough mixture of the different metals the melted mass should be poured from a height into a vessel of cold water, and this process of granulation should be repeated at least three times, but at every melting the alloy should be well covered with borax to prevent loss of the tin by oxidation. The vessel into which the melted mass is poured should not be a metallic one.

The component parts of the alloy having now been thor-

oughly incorporated, the next step is to collect the granulated mass and separate from it any adherent particles of glass or borax. The metal is then put into a glass or porcelain evaporating dish (the Berlin porcelain is the best), and sufficient chemically pure nitric acid is added to cover the metal. The dish is now placed over a sand-bath, and gentle heat applied and continued until chemical action ceases. If at this point it is found that all the metallic particles are dissolved, the dish may be removed from the bath. Should any solid particles be found in the solution, a little more nitric acid must be added and the operation continued until all are dissolved. The silver having been entirely dissolved by the nitric acid, the solution should be poured off, and the remaining oxide carefully washed until the last trace of silver is removed. After several washings with a large quantity of pure warm water, the latter should finally be tested with a clear solution of common salt, and if it remains clear, without show of milkiness, the silver is all removed. When the oxide is sufficiently washed the purple of Cassius should be dried by gently heating, after which it is ready to be incorporated with the silicious materials.

Compounds of Gold.—Gold forms two series of compounds: aurous and auric; in the first it has a valancy of one, while in the second it is trivalent. The aurous compounds are very unstable.

It forms two oxides: aurous, Au_2O and auric, Au_2O_3 . Aurous oxide is very unstable and when treated with dilute hydrochloric acid, auric chloride is formed. When heated to 250°C . it decomposes with the liberation of metallic gold. It is a violet-colored powder. Auric oxide acts both as a feeble acid and as a basic oxide. It is a brown powder and when treated with water and heated, forms $\text{Au}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, or $\text{Au}(\text{OH})_3$. At 100°C . it begins to decompose into gold and oxygen. As a basic oxide it forms a few unstable salts with certain acids in which gold replaces the hydrogen of the acid. As an acid oxide it combines with certain metals, forming aurates. With ammonia this compound forms an explosive substance, fulminate of gold.

Chlorides of Gold.—Gold forms two principal chlorides: aurous chloride, AuCl , and auric chloride, AuCl_3 .

Aurous Chloride.—Aurous chloride is formed when auric chloride is heated to 180°C . It is a white powder, insoluble in water, but upon boiling is converted into auric chloride and free gold is liberated.

Auric Chloride.—Auric chloride is obtained by treating gold with aqua regia or chlorine and evaporating to dryness. When the residue is dissolved in water the concentrated solution deposits reddish crystals of the composition $\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$. Auric chloride forms compounds with alkali salts and also with hydrochloric acid, the latter may be represented by the formula, $\text{AuCl}_3 \cdot \text{HCl}$ or HAuCl_4 , known as chlorauric acid. This compound is deposited from a strong solution of gold in aqua regia in crystalline form, having the composition $\text{AuCl}_3 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$.

Gold does not form sulphides in the dry way but may be precipitated from solution of a soluble salt by hydrogen sulphide.

Two sulphides have been obtained in this way, aurous, Au_2S , and auro-auric, Au_2S , Au_2S_3 or $4(\text{AuS})$.

Fire Assay for Gold and Silver.—The following method is one of many that may be used in determining the quantity of gold present in an ore. The system of weights used are so constructed that the same ratio exists between the assay ton weight and a milligram as between an ounce and a ton. There are 29166 Troy ounces to a ton, and an assay ton weighs 29.166 grains; then on comparison there are 29166 milligrams to the assay ton and the ratio between 1 milligram and an assay ton is as 1 to 29166, which is the same as the Troy ounce to the ton.

The weight of the gold bead obtained from an assay will then represent the number of ounces of gold to the ton of ore.

A high-grade gold ore is one that contains five dollars or more of gold to the ton of ore, that would equal about 0.242 ounce and the gold bead weigh 0.242 milligram.

Procedure.—If the ore contains sulphur it must be desulphurized by roasting. To facilitate this process, iron nails

are sometimes added to the ore, to assist in taking up the sulphur.

The ore is next submitted to the crucible process. A charge is prepared, consisting of the following:

Ore	1	assay ton
Sodium bicarbonate	1½	" "
Potassium carbonate	½	" "
Litharge	1½	" "
Silica	1	" "
Borax glass	½	" "
Charcoal	$\frac{1}{10}$	grain.
Salt to cover.		

The charge is placed in a Battersea crucible of suitable size and then introduced into the furnace. The litharge is reduced to metallic lead, which then dissolves the gold and silver from the ore and the salt covering and fusible slag formed prevent the oxidation of the reduced metals. After the charge has been in the furnace for about twenty minutes, the crucible is removed and the lead is poured into a suitable mold. The lead button obtained from this process usually is too large for direct cupellation; to reduce the size of same it is submitted to a scorification process.

The lead is hammered into the shape of a cube and then weighed, the average cupel can take care of a lead button weighing 25 grams; however, if it weighs more than this amount the button is placed in a scorifier and covered with borax. The scorifier is then placed in a muffle furnace and the lead oxidizes. When sufficient lead has been removed the molten mass is again poured into an ingot mold. The lead is freed from the slag and again hammered into a cubical form and is ready for cupellation.

A cupel is constructed of bone ash; sometimes a little sugar is added so as to make the mass more porous. The cupel is placed in the muffle furnace and heated until all of the lead has been removed. This point may readily be perceived by a peculiar phenomenon which takes place in the molten metals. The button of silver, gold and lead appears to revolve with great velocity, and rainbow colors succeed one another over its surface. Finally a film passes over the

bead, and then no more action is visible. This point is known as the "blicking point." The bone ash of the cupel possesses the property of absorbing lead oxide and thus keeps the button free from this agent. The cupel is removed from the furnace and the button weighed, it is then subjected to the parting process. The parting process is dependent upon the solubility of silver in a 1-to-3 gold-silver alloy in nitric acid. The color of the button is an indication as to the quantity of gold present, and if there is evidence that there is not sufficient silver in the button, more silver may be added.

The button is then flattened and placed in a flask, nitric acid, specific gravity 1.2, is added. The flask is heated until all chemical action ceases; the liquid is then filtered and the gold collected and weighed. The difference between the weight of gold and the weight of the button received from the cupel is the weight of silver.

RESUMÉ.

Symbol, Au.	Crystalline form, isometric.
Valency, I to III.	Chief ore, native metal.
Atomic weight, 197.2.	Conductivity of heat, 532.
Melting point, 1120° C.	Conductivity of electricity,
Specific heat, 0.0324.	72.55.
Boiling point, 2200° C.	Coefficient of expansion,
Color, yellow.	0.00001466.
Malleability, 1st.	Ductility, 1st.
Specific gravity, 9.3 to 191.5.	Tenacity, 5th.

CHAPTER XVI.

PLATINUM.

Symbol, Pt. Atomic weight, 195.2.

Occurrence.—Platinum occurs in nature in but few minerals. The principal source is from native platinum, which also carries iron, palladium, osmium, rhodium, iridium and copper as impurities. It also occurs as the arsenite, PtAs_2 , sperrylite, and as impurities in iridosmium, IrOs . The greater part of the world's supply is obtained by washing placer deposits in the Ural Mountains. The gold placers in Columbia, South America, is the second district of importance in the production of platinum, although it furnishes only about one-twentieth of the quantity obtained from Russia. A valuable deposit has recently been reported in Spain. Platinum is found in nature as flattened grains of the native metal containing about 51 to 86 per cent. platinum. The only native compound, sperrylite, is found at Sudbury, Canada, as impurities in the nickel-bearing pyrrhotite and calcopyrite and also in the cupric sulphide occurring in Wyoming.

Historical.—The first mention of platinum was by Antonio de Ulloa, a Spanish naval officer, in a book published in 1748. In his narrative he mentions the finding of platina (Spanish diminutive of plata, silver) in the Choco District of Columbia in which it is admixed with gold. Ulloa is given credit for the introduction of platinum in 1735. Wood a few years later, 1741, also makes mention of this metal.

Platinum was at first considered an objectionable metal, because it interfered with the working properties of gold. Watson, in 1750, and Scheffer, 1752, were the first to describe the metal. The German chemist Margraf was the first investigator to obtain platinum in a fairly pure condition.

He obtained the metal by acting upon platinum chloride with potassium and sodium salts and then upon heating obtained spongy platinum. In 1819 platinum was discovered in the Ural Mountains. Wollaston next introduced a method of obtaining malleable platinum from the pure spongy metal, but the great difficulty to be overcome was to fuse it in large quantities. Deville and Debray, in 1858, devised a process by which large quantities of the metal can be melted.

Reduction.—*Wollaston's Process.*—The ore is first washed and then treated with hydrochloric acid; this dissolves the base metals. The ore is next treated with aqua regia, which dissolves palladium, rhodium, platinum and a little iridium as the chlorides. The osmium in the ore partly distils over as osmium peroxide and partly remains undissolved as an alloy with the iridium, together with ruthenium, chrome iron ore and titanite iron. The proportions of acids are one hundred and fifty parts hydrochloric to forty parts of nitric. Three or four days are necessary to dissolve the ore, aided by gentle heat. The solution containing the platinum is neutralized with sodium carbonate and the palladium is precipitated as cyanide, $\text{Pd}(\text{CN})_2$, by the addition of mercuric cyanide. The platinum, is next precipitated by adding ammonium chloride with the formation of yellow crystalline ammonio-platinic chloride, $(\text{NH}_4)_2\text{PtCl}_6$. If rhodium is present, it must be removed at this stage. Its presence will manifest itself by the solution from which the platinum has been precipitated, changing to a rose color. This rose color solution may also contain about 11 per cent. of the platinum. Rhodium may be recovered by mixing the precipitate with potassium acid sulphate, KHSO_4 , and heating to redness in a platinum crucible. The rhodium is converted into rhodium potassium sulphate, which may be removed from the spongy platinum by dissolving with boiling water. The 11 per cent. of platinum in the mother liquor is treated with zinc strips which precipitates the platinum with the other metals present. A small quantity of strong hydrochloric is added to avoid precipitating lead or palladium, when the remainder of the platinum is thrown down with ammonium

chloride. The ammonium chlorplatinate is thoroughly washed in cold water, to remove iridium, which also forms a double salt with ammonium chloride. The next stage in the operation consists in separating the metal from the ammonium salt by ignition, and, as it is important to the success of the subsequent working that the precipitate shall remain in a finely divided state; too high a degree of heat must be avoided, as otherwise cohesion of the particles will take place. Ignition is generally accomplished by the following means: The precipitate is heated in a graphite crucible until nothing remains but the finely divided platinum. This is powdered, should it be found somewhat lumpy, in a wooden mortar with a wooden pestle, sifted through a fine lawn sieve, and mixed with water to the consistency of a paste. This is placed in a brass mold with a slightly tapering cylindrical cavity about seven inches in length, provided with a loosely fitting steel stopper, which enters to the depth of a quarter of an inch. The mold is first oiled and set up in a vessel of water. The platinum mud is then introduced, and as it settles into the water, air is displaced, and the platinum is thus made to fill every part of the mold. The water is allowed to drain, and its removal may be aided by pressure. Ultimately, however, the mold is placed in a press worked by a powerful lever, by which the mass sustains an enormous pressure, after which the plug and the column of platinum are removed by gently tapping the mold. It is then heated in a charcoal fire, in order to thoroughly dry it and to burn off any adherent oil.

The next step, which depends upon the quality of welding possessed by platinum, consists in heating the porous cylinder in a blast furnace to white heat, when it is removed, set upright on an anvil, and hammered on the ends, in order to weld the particles; after which it is coated with a mixture of borax and carbonate of potash, and again heated for the purpose of removing traces of iron, which are dissolved by the mixture, the latter being removed by immersion in dilute sulphuric acid. The bar of platinum is now ready for use, and may be rolled or hammered.

It may readily be surmised that so imperfect a means of obtaining a solid bar of metal as the latter part of the operation just described cannot always be relied upon for the production of a uniform and solid specimen; and, indeed, platinum prepared in this way, though of great purity, is liable to blister upon its surface, this being probably due to minute bubbles of air encased in the body of the ingot during the forging, which during the conversion of the ingot into plate by means of rollers, are elongated and spread out in the form of blisters.

Deville and Debray Process.—The dry metallurgical operations of Deville and Debray consist in heating in a reverberatory furnace about two hundred pounds of platinum ore with an equal weight of galena (lead sulphide). When the ore is sufficiently heated (to bright redness), portions of the galena are added and mixed with the ore by constant stirring. An equal quantity of litharge is next added, in order to supply oxygen to the sulphur of the lead ore, which passes off as sulphurous anhydride, reducing all of the lead which combines with the platinum. After remaining in a state of fusion for a short time the upper portion is ladled off, and will be found to consist of an alloy of lead, platinum, and smaller portions of palladium and silver, the latter being introduced from the galena, which always contains more or less silver. The heavier metals of the platinum group, by their greater density, subside to the bottom.

Cupellation is now resorted to in order to separate the platinum from the lead. This consists of two distinct operations. The first is performed at the ordinary furnace temperature, and is continued until by loss of lead the fusing point of the remaining alloy rises to such an extent that a state of fusion can no longer be maintained. The second and final operation is performed in an apparatus which serves the purpose of both furnace and cupel. It is formed of blocks of thoroughly burned lime. In form it may be described as a sort of basin or concavity, with a similar piece for a cover. The lower part is intended for the reception of the metal; through the center of the upper portion or cover

pass the tubes for the oxhydrogen jet, while the lower portion is divided with a lip or spout for pouring the melted metal. The tubes which pass through the top for the transmission of the two gases are generally formed of copper, with platinum tips. The outer and lower tube carries hydrogen, while the inner and upper one carries a jet of oxygen into the middle of the flame. The tubes are furnished with stopcocks so that the supply may be regulated. When the object is merely to fuse some scraps of platinum the lime furnace is first put together, the hydrogen jet is lighted, oxygen is then turned on, and the interior of the apparatus soon becomes heated. The platinum is then introduced in pieces through a small hole at the side, and quickly fuses after entering the furnace.

When used as a cupel the lime absorbs the impurities and the platinum is kept in a state of fusion until all the lead is oxidized, when the metal may be poured from the lime cupel into an ingot mold formed of coke or plates of lime. Some difficulty may be experienced at the moment of pouring, in consequence of the dazzling white surface of the molten metal. From seven to eight pounds may be melted in this way in from forty to sixty minutes.

Although such metals as palladium, osmium, gold, silver, and lead are volatilized at the intense heat used, it has been found that platinum obtained by the Deville-Debray method is not as pure as that obtained by Wollaston's plan.

Properties.—Platinum is a tin-white metal, softer than silver but is hardened by the admixture of other metals, especially iridium. It is surpassed in malleability by gold and silver, but in ductility it in all probability stands first. Wollaston succeeded in drawing it out into a wire $\frac{1}{30000}$ of an inch in diameter, while the smallest gauge of gold wire that has been reported is $\frac{1}{50000}$ of an inch. Platinum is more tenacious than gold, and as tenacity has a direct influence upon ductility it is more than probable that platinum is more ductile than gold. Platinum possesses about the same coefficient of expansion as glass; this property renders it invaluable to dentistry and the arts. When platinum is

baked in porcelain, and the mass cools, it will be found that platinum contracts at the same rate as the porcelain, thus insuring an absolutely tight joint. In the manufacture of incandescent globes, platinum is used where the filament penetrates the glass. The globe is a partial vacuum, and any other metal will be found to contract, upon cooling, at a different rate from the glass and thus forming an imperfect joint, leakage would result and the vacuum be destroyed. Because of the recent abnormal price of platinum, substitutes have been offered the dental profession; a substitute to be of value should possess the following qualities in order to be of service:

1. It should possess a high fusing point.
2. It should have about the same coefficient of expansion as platinum.
3. It should be able to withstand the action of chemical substance.
4. It should be easily soldered.
5. The price should not be prohibitive.

Platinum fuses at about 1753° C. Small quantities may be fused with the oxyhydrogen blow-pipe, but in large quantities fusion is usually accomplished by the use of a lime furnace and a powerful oxyhydrogen blow-pipe (Fig. 50).

Platinum does not combine with oxygen at any temperature, nor does it absorb this gas, but in the cold it condenses oxygen upon its surface. A piece of platinum foil, when introduced into a mixture of oxygen and a readily inflammable gas, causes them to combine. This action is more rapid in the case of platinum sponge, where a larger surface is brought into play, and a fragment of this material introduced into a detonating mixture of oxygen and hydrogen at once causes it to explode.

Platinum may be welded at white heat, and vessels made of platinum may be repaired in this manner. In the finely divided state it may be made into small vessels by pressing the powdered mass of platinum into suitable molds, heating and hammering to complete the welding of the particles.

Platinum is a very poor conductor of electricity, and when

a current is passed through a platinum wire of small diameter the resistance offered to the flow of the electric current is so great that the wire becomes hot and glows; advantage is taken of this in the construction of the small electric furnaces used in dentistry. The heating element consists of a platinum loop imbedded in the fire-clay lining. The electric switch-boards have a platinum electrode used as a root-canal dryer. Electric annealers, sterilizers and various other forms of

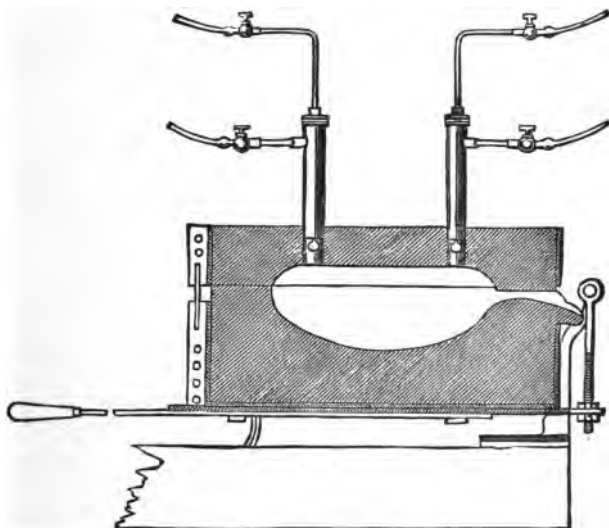


FIG. 50

electrical contrivances also make use of platinum in the same capacity. In the electromotive series, platinum with gold are the most electronegative of the metals, and metals which dissolve but slowly in acids are more rapidly acted upon when placed in contact with platinum, forming a so-called platinum couple. Solutions of antimony when placed in hydrochloric acid and a zinc platinum couple is introduced into the acid, the zinc is rapidly attacked and the antimony is deposited upon the platinum. In chemical reactions, platinum and its

salts possess a peculiar property of facilitating chemical action without being acted upon themselves; in other words, it acts as a catalytic agent. In the manufacture of sulphuric acid by the contact process, platinum salts cause an oxidation of sulphur dioxide to the trioxide by its mere presence, illustrating the catalytic action of platinum salts.

Platinum black is platinum in an exceedingly fine state of subdivision formed when platinum is precipitated from solution by reducing agents or metals. It is a soft, black powder, which is capable of absorbing enormous quantities of oxygen. Platinum black absorbs about eight hundred times its volume of oxygen, no chemical union taking place, and hence it acts as a very powerful oxidizing agent.

Platinum readily combines with phosphorus, silicon and carbon. The carbide of platinum is formed when the metal is continuously heated by a smoky flame or one in which combustion is incomplete.

Compounds.—There are two oxides of platinum: platinous oxide, PtO , and platonic, PtO_2 .

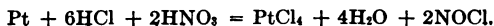
Platinous oxide is formed when platinous hydroxide is boiled. It is a black powder, easily soluble in hydrochloric acid.

Platonic oxide is formed by gently heating platonic hydroxide. It is a black or grayish-black powder. When strongly heated both of these oxides are reduced to metallic platinum.

Platinum forms two chlorides: platinous, PtCl_2 , and platonic, PtCl_4 .

Platonic chloride is formed by treating platinum with aqua regia; if this be heated to 250° platinous chloride will be formed. The platinum salts possess the property of combining with others, forming double salts. With ammonium or potassium chloride the resulting compounds are insoluble in water.

Solubilities.—The best solvent for platinum is aqua regia, with the formation of platonic chloride. The reaction may be represented as follows:



It is not as readily acted upon by these acids as is gold. Platinum is not affected by water or by air at any temperature; it is not sensibly tarnished by hydrogen sulphide, nor is it attacked by sulphuric, by hydrochloric or nitric acids.

Silver alloyed up to 10 per cent. of platinum is attacked by nitric acid; any larger proportion of platinum will remain undissolved. Platinum is also attacked by fusing with caustic alkalies and alkali nitrates, so care should be used not to fuse these compounds in platinum vessels

Alloys.—Gold and platinum alloy and the resultant alloy has a greater coefficient of elasticity than either metal. In dentistry this alloy is used for clasp metal and also for casting in crown and bridge-work. Fenchel quotes Bornemann, that the hardness steadily increases with 20 to 30 per cent. platinum, when it equals that of pure platinum, and then increases up to 50 per cent., when the hardness equals that of calcareous spar. It then falls again to the platinum level. An excess of platinum renders the alloy infusible in the ordinary furnace. The tenacity of gold is increased while the malleability is somewhat impaired. The color of the alloy is not so brilliant as that of gold when equal parts of the two metals are alloyed. Foils of so-called platinous gold are also used for a filling material; this so-called platinous gold possesses hardness, but it is more difficult to work and the color is objectionable to some individuals.

Platinum solder usually contains from fifteen to twenty-five parts of platinum alloyed with gold. Pure gold is also used in soldering platinum; a minimum amount of gold is used and any excess should be driven off by heating, especially in joints to be covered by porcelain, as there is a liability of the excess gold volatilizing at the high temperature of the porcelain furnace which would result in gassing the porcelain.

Silver and platinum alloy in all proportions, forming alloys which are harder than silver, and the color is between that of silver and platinum. The alloy is hardly more resistant to the action of reagents than pure silver. Hot sulphuric and nitric acids attack it. An alloy containing about 25 to 30

per cent. of platinum is known as "dental alloy" and has been used in Europe for making dental bases.

Mercury and platinum do not amalgamate readily. Finely divided platinum when rubbed with mercury in a heated mortar produces this amalgam; the amalgamation may be facilitated by moistening the platinum with dilute acetic acid.

Iron and platinum unite to form an alloy, and for this reason care should be taken not to contaminate platinum with iron. The alloy has a lower fusing point than platinum, and if iron should come in contact with a platinum piece it will result in the fusing of the alloy and thus burn a hole in the platinum.

Iridium and platinum are alloyed to produce an alloy possessing rigidity, high fusing point and great resistance to the action of chemical agents. The principal uses of this alloy in dentistry are for the construction of dowels and bars in crown and bridge-work.

Tin and platinum alloy in all proportions, forming alloys which are hard and brittle and more or less fusible.

Lead and platinum alloy readily, and the alloy has a much lower fusing-point than platinum.

Tin and lead alloys with platinum may be fused in the Bunsen burner. When swaging a piece of platinum, using the base metals lead or tin, great care should be exercised not to contaminate the platinum, for the alloys formed during the annealing process would readily fuse and thus ruin the piece.

Melting Platinum Scraps.—As has been already described, the oxyhydrogen blow-pipe may be used; it is also claimed that the oxyacetylene blow-pipe proves very efficient for melting platinum. Dr. Prothero in his late work on *Prosthetic Dentistry*, describes a method gotten up by Dr. L. E. Custer, of Dayton, Ohio, in which the electric current is used.

There are two forms of melting devices: 1. The current from the positive pole is attached to a wire capable of carrying a 110-volt current and this is then connected with a carbon block, the negative charge is conveyed to a brass electrode

surrounded with a wooden handle. The platinum obtained by fusing with this form of a device is harder than new platinum because of the absorption of small quantities of carbon from the block.

2. In this form of melting device a lime block is used, a piece of heavy platinum wire is so shaped as to form a receptacle for the platinum scraps; this wire is attached to the positive terminal. The negative terminal is attached to a brass rod having a slit in its exposed surface, in which a platinum ingot of about one-half ounce weight is fastened. The arc is established by placing a carbon pencil between the terminals. (For complete description, see Prothero's *Prosthetic Dentistry*, pp. 1070 and 1071).

Methods of Separating Platinum, Gold, Silver and Base Metals.—If possible, fuse the scrap metal, and while in the fused condition pour into water from a height, or the fused metal may be rolled out and then cut up into small pieces. The object of this procedure is to facilitate the solution with aqua regia. The alloy so prepared, or if the scraps are infusible in the blow-pipe flame, the original scraps are treated with aqua regia (consisting of three parts of hydrochloric acid and one part nitric acid). The reaction should be carried out in a porcelain dish of sufficient size to hold the excess of aqua regia needed to dissolve the metals. Place the dish upon a water-bath and heat, when the reaction has ceased, dilute with an equal quantity of distilled water and filter. This partially removes silver as the chloride; antimony and tin as the oxides. Wash the precipitate thoroughly with distilled water and then evaporate the solution to dryness on the water-bath. Dissolve the residue in distilled water and allow to stand for a few hours. Any silver remaining will settle, and by decanting and filtering the silver may be completely removed. The gold may be precipitated next by warming the solution and adding oxalic acid; filter after the gold has been precipitated, and again evaporate to dryness; place in a hood and heat for some time to expel the excess of oxalic acid. Treat the residue with aqua regia, boil off excess of acid then add sodium carbonate solution until the

solution is nearly neutral, the platinum may then be precipitated by adding ammonium chloride solution. Collect the precipitate on filter paper, wash and then heat and the platinum will be obtained in the finely divided state. It can be fused in the oxyhydrogen blow-pipe flame.

RESUMÉ.

Symbol, Pt.	Crystalline form, isometric.
Valency, II or IV.	Chief ore, iridosmium.
Atomic weight, 195.2.	polyxene.
Melting point, 1753° C.	Conductivity of heat, 84.
Specific heat, 0.0324.	Conductivity of electricity, 14.6.
Boiling point, very high temperature.	Coefficient of expansion, 0.000008.
Malleability, 6th.	Ductility, 1st (3d).
Color, white.	Latent heat of fusion, 27.18 calories
Tenacity, 3d.	
Specific gravity, 21.5.	

CHAPTER XVII.

OSMIUM, IRIDIUM, PALLADIUM, RHODIUM, AND RUTHENIUM.

THESE metals with platinum comprise the so-called platinum group. Considering the properties possessed by these metals they may be subdivided into two distinct groups. Osmium, iridium and platinum consisting one subgroup and rhodium, ruthenium and palladium the second. The following chart illustrates some of the properties of these metals:

	Atomic weights.	Specific gravity.	Fusing points.	Solubilities.
Osmium . . .	190.9	22.48	2500° C.	Compact metal insoluble in all acids.
Iridium . . .	193.1	22.42	2300	Fused metal insoluble in all acids.
Platinum . . .	195.2	21.5	1753	Solution in aqua regia.
Rhodium . . .	102.9	12.1	1546	Insoluble in acids.
Ruthenium . . .	101.7	12.26	next to osmium	Aqua regia with difficulty.
Palladium . . .	106.7	11.5	1500	HCl, H ₂ SO ₄ , HNO ₃ .

OSMIUM.

Symbol, Os.

Osmium is the heaviest of all bodies. It may be heated above the boiling point of platinum without melting when air is excluded. When heated to about 415° C. in the presence of air the volatile and poisonous perosmic oxide (acid), OsO₄, is formed. In compact form osmium is very hard, cutting glass, and possesses a metallic luster resembling zinc in appearance. It occurs in nature as osmiridium. The metal in compact form is not attacked by any acid. The precipitated metal is slowly dissolved by nitrohydrochloric or fuming nitric acids. Osmic acid is used in staining specimens for histological work.

IRIDIUM.

Symbol, Ir.

Iridium derives its name from iris, the rainbow, because of the color of its various compounds. It occurs as an insoluble compound in the reduction of platinum ores, being insoluble in nitrohydrochloric acid. This alloy, osmiridium, left after treating the platinum ore with aqua regia, is mixed with sodium chloride and heated in a stream of chlorine and a double chloride of the metal with sodium results. The mass is extracted with boiling water. The solution is then evaporated and distilled with nitric acid, and osmium is distilled off as the peroxide. Upon adding ammonium chloride to the solution in the retort iridium is precipitated as ammonium chloriridate, $(\text{NH}_4)_2 \text{IrCl}_6$, as a dark, red-brown precipitate, and this compound upon heating leaves metallic iridium as a spongy mass. Spongy iridium oxidizes readily when heated in air, excluding air the iridium may be fused in an oxygen-hydrogen blow-pipe giving a brittle mass which does not oxidize upon heating in air. It is not attacked by aqua regia unless in the finely divided state.

Iridium may also be obtained by treating the platinum residues with lead and lead oxide and heating to redness for one-half hour. The alloy is then treated with sodium chloride and chlorine as described before.

Properties.—Pure iridium scarcely melts in the oxygen-hydrogen flame and can be worked only with difficulty; however, at red heat it is somewhat malleable. It is rather hard metal, having a hardness about equal to slightly tempered steel. Iridium forms compounds having a valency of two, three, and four. The metal combines with carbon with the formation of iridium carbide, IrC_4 . The metal in a finely divided state dissolves in nitrohydrochloric acid with the formation of the chloride. Its best solvent is chlorine. When fused with potassium acid sulphate it is oxidized, the same results may be obtained by fusing with sodium hydroxide or sodium nitrate and the oxide in the latter cases is partially soluble in the excess of the alkali. When solutions of iridium

salts are treated with formic acid a deep black powder is formed. This powder when incorporated with fluxes and oils is used as a paint for porcelain work; upon fusing it produces a very fine black.

Iridium is used in springs of fine watches and clocks because of its non-magnetic properties.

Alloys.—Platinum containing a small quantity of iridium is rendered more rigid.

In the laboratory vessels made of this alloy frequently scale because of the oxidation of the iridium. Iridoplatinum is used in dentistry for dowels in crown and bridge-work and also as a means of strengthening continuous gum work. The best solder for this alloy is pure gold. Gold alloys with iridium, forming a workable alloy, while silver is said to be immiscible with it. An amalgam may be produced, but it does not possess any properties of value.

Compounds.—Iridium forms four oxides: IrO , Ir_2O_3 , IrO_2 , and IrO .

Four chlorides are known: iridium dichloride, IrCl_2 ; iridium trichloride, IrCl_3 , and iridium tetrachloride, IrCl_4 . Hydrogen sulphide reduces iridium tetrachloride to the trichloride and then precipitates the bisulphide Ir_2S_3 brown, soluble in alkali sulphides.

Stannous chloride, ferrous sulphate and oxalic acid reduces iridium to compounds having a valency of three, but does not reduce them to the metallic condition.

RHODIUM.

Rhodium occurs associated with platinum. It is obtained from the solution of the ore in nitrohydrochloric acid by precipitating the platinum with ammonium chloride, neutralizing with sodium carbonate, adding mercuric cyanide to separate palladium, filtering and evaporating the solution to dryness in the presence of hydrochloric acid. The residue is treated with alcohol and rhodium is obtained as a red powder as the double chloride of rhodium and sodium. This compound is heated in a tube and a gray powder of metallic

rhodium is obtained when the residue is washed with water to remove the sodium chloride. When fused in the oxyhydrogen blow-pipe it becomes a hard, brittle metal. Pure rhodium is a white metal said to be nearly as malleable and ductile as silver. It may be obtained by being precipitated from solution with alcohol or formic acid.

The pure metal or the alloys with gold or silver is almost insoluble in acids; according to Deville and Delroy, the alloys with bismuth, lead, copper, or platinum are soluble in nitric acid.

RUTHENIUM.

According to Gibbs, ruthenium may be obtained from platinum ores by mixing the platinum residues with sodium chloride then igniting in a stream of chlorine gas. Dissolve the fused mass in water and add potassium nitrate, neutralized with sodium carbonate and then evaporate to dryness, extract the double nitrates formed with absolute alcohol, this precipitates the rhodium. Add water to the solution, distil off the alcohol, and then add hydrochloric acid and the ruthenium is precipitated as potassium ruthenium chloride. This salt is then converted into the ammonium salt and upon adding mercuric chloride upon recrystallizing and igniting pure ruthenium is obtained.

Ruthenium has an exceedingly high melting point. It can be melted in the electric arc and it is then a gray and very hard metal; though brittle when cold, it becomes malleable; when hot it has a specific gravity of 12.26 and is insoluble in acids, except nitrohydrochloric in which it is slightly soluble.

PALLADIUM.

Symbol, Pd.

Occurrence.—Palladium is nearly always present in platinum ores. It also is found with gold and silver. In the native state small quantities are found in Brazil. Palladium was at one time extensively used in dentistry for the construction of metallic bases for artificial dentures; however, the

price of this metal has advanced so greatly that its use was discontinued.

Reduction.—The native alloys containing palladium is fused with metallic silver and then treated with nitric acid which leaves gold undissolved. The silver is precipitated by adding a chloride and the filtered solution is then treated with mercuric cyanide and palladium cyanide is thrown out of the solution; when the cyanide is heated spongy palladium is obtained. Spongy palladium may be welded into form the same as platinum.

Properties.—Palladium resembles silver in appearance and is whiter than platinum. It is softer than platinum and may be hammered into sheets or drawn into wire. It conducts electricity about one-eighth as well as silver. When the metal is slightly heated it assumes a rainbow tint from green to violet. In air at the ordinary temperatures, especially the spongy form does not tarnish, but at a higher temperature, red heat, it becomes coated with an oxide; at a still higher temperature the oxide is reduced.

Hydrogen sulphide does not attack the metal, consequently palladium does not tarnish like silver. It may be distinguished from platinum by treating with an iodine solution; the platinum will not be attacked while palladium forms a black compound, PdI_2 .

Palladium in spongy form absorbs large quantities of hydrogen. It occludes hydrogen even at ordinary temperatures, and at 100°C . it takes up about nine hundred and sixty times its volume of hydrogen. When heated in oxygen it takes up this gas which is again given off in the same manner as silver under a like condition, and spitting occurs during the act of solidification.

Solubilities.—Boiling hydrochloric or sulphuric acids slowly dissolves the metal, while nitric acid, even in the cold, readily attacks palladium with the formation of the nitrate $\text{Pd}(\text{NO}_3)_2$. An alcoholic solution of iodine blackens it, and when fused with potassium hydrogen sulphate, palladium is attacked with the formation of the sulphate, both of these reactions distinguish palladium from platinum.

Compounds.—Palladium forms three oxides: Pd_2O , PdO , and PdO_2 .

Palladium monoxide, PdO , is the most stable oxide of palladium. It is formed by gently igniting the nitrate $\text{Pd}(\text{NO}_3)_2$ or by treating palladous chloride, PdCl_2 , with sodium carbonate, forming palladous hydroxide, $\text{Pd}(\text{OH})_2$, and then igniting.

Alloys.—*Gold and Palladium.*—These alloys are light in color and much harder than pure gold. According to Prothero the alloys of these two metals which he has investigated (1 to 30 per cent. palladium) were perfectly uniform, malleable, ductile, and tenacious. Silver and palladium unite in all proportions, forming exceedingly brilliant alloys.

Platinum and Palladium.—Platinum and palladium form hard alloys which melt below the fusing point of palladium.

Palladium combines with antimony, bismuth, zinc, tin, iron, lead, and nickel.

CHAPTER XVIII.

IRON.

Symbol, Fe (ferrum). Atomic weight, 55.84.

Occurrence.—Next to aluminum, iron occurs in the greatest abundance of all the metals. In the free state iron is found present in meteorites. The minerals of iron are of importance:

1. For the extraction of metal (ores of iron).
2. For the extraction of acid constituents.
3. For the extraction of metals present as impurities in the iron minerals.
4. For use in their native state.

The minerals of iron included under (1) and their descriptions follow: Hematite, specular iron, red iron ore, is the principal working ore of iron. It contains about 70 per cent. of iron. About 72 per cent. of the iron ore mined in the United States is hematite. The hematites are characterized by giving a red streak.

Limonite ranks second, and the cause of this is, it requires more fuel to reduce this ore of iron than the hematites. Hematites subjected to the influences of water become hydrated and their color changes from red to yellow. Limonites give a yellow streak and may be represented by the formula $\text{Fe}_2(\text{OH})_6\text{Fe}_2\text{O}_3$. They contain about 59.8 per cent. iron.

Magnetite, Lodestone, Magnetic Iron Ore.—This ore is not very prevalent in the United States; however, it is practically the only source of iron in Sweden. It produces a very high grade of iron, and the noted Swedish steel is manufactured from this source of iron. It contains about 72.4 per cent.

Siderite the carbonate of iron, FeCO_3 , is made use of in the production of iron, although it makes up only 1 per cent. of the iron ores reduced in the United States.

The minerals included under (2) are: (a) For the recovery of sulphur.

Pyrites, FeS_2 ; marcasite, FeS_2 ; pyrrhotite, $\text{Fe}_{1-x}\text{S}_{2+x}$

These ores are roasted and the sulphur dioxide is used in the manufacture of sulphuric acid. Because of their high sulphur content it is generally not considered practicable to reduce these ores for their iron. The residues from the roasting frequently contain copper, nickel or gold which are recovered later.

(b) For arsenic, arsenopyrite, FeAsS , is the principal source of arsenic.

(c) For chromium, chromic iron, FeCr_2O_4 , is the chief source of chromium.

(d) For tungsten wolframite, $(\text{FeMn})\text{WO}_4$. This mineral together with scheelite, (CaWO_4) , are the principal natural occurring compounds of tungsten.

Minerals Included Under (3).—Gold and silver are recovered from pyrite and arsenopyrite, and nickel from pyrrhotite.

Minerals Included Under (4).—The natural oxide paints are obtained from this source. Limonite and hematite are the principal minerals used. Ochre, umber, sienna are the pigments produced. Rouge, used in polishing gold is obtained from this source, as is also crocus martis which is used in medicine.

Historical.—Iron, though the most common of metals, was in all probabilities not made use of until after the introduction of gold, silver, copper, tin, and mercury. It is certain that it was prepared in ancient Egypt, and at a very remote epoch. It was little used in Greece until after the Trojan War. The Greeks ascribe the discovery of iron to themselves; but Moses relates that iron was wrought by Tubal-Cain. Iron furnaces among the Romans was not fitted with a bellows but were located on eminences with the grate in the direction of the prevailing winds. The Arundelian marbles state that iron was found on Mount Ida, by Doctyles, owing to the forests of the mount being burned by lightning, B.C. 1432.

Mills for rolling and cutting iron were first introduced in 1590, and tinning iron in 1681. The first mention of casting iron in England was in 1543. Quoting from Dr. Ure: "Iron accommodates itself to all our wants and desires, and even out caprices. It is equally serviceable to the arts, the sciences, to agriculture and war. The same ore furnishes the sword, the plowshare, the scythe, the pruning-hook, the needle, the graver, the spring of a watch or of a carriage, the chisel, the chain, the anchor, the compass, the cannon and the bombs. It is a medicine of much virtue and is a constituent of both animal, vegetable and mineral kindgom."

Reduction.—Iron chemically pure is produced by reducing pure iron oxide with hydrogen; this is called "iron by hydrogen." At the present time practically all iron is prepared by the blast-furnace process. The crude iron ore is first subjected to mechanical treatment, which consists of crushing the ore, then the earthy impurities are partially removed by washing.

The washed ore is next roasted; in this process sulphur, carbon, and moisture are driven off, and sometimes the ore becomes more magnetic. The next process consists of magnetic concentration of the mass; this has a tendency to free the ore of earthy impurities which have been broken up during the crushing process. The ore may then be treated with some binding material and pressed into briquettes and is ready for the blast furnace.

The Blast Furnace (Fig. 51).—The blast furnace consists of a vertical shaft, forty to eighty feet high, having the shape of a truncated ellipse, with the widest diameter varying from ten to twenty-four feet, about one-fourth of the height. At the bottom of the furnace is the hearth diameter, four to eight feet, in which the molten iron collects; this is perforated by several openings or tuyères, through which the air blast enters the furnace. The hearth has also two other openings: the lowermost one for the escape of the iron is known as the tap hole; the second (slag hole), at a higher level, through which the slag is allowed to run out.

The top of the furnace, called the throat, diameter four

to eight feet, is closed by the bell, which is a cone-shaped arrangement for collecting the gases; these then are carried away by the downcast and used as fuel for heating the air to be used in the blast.

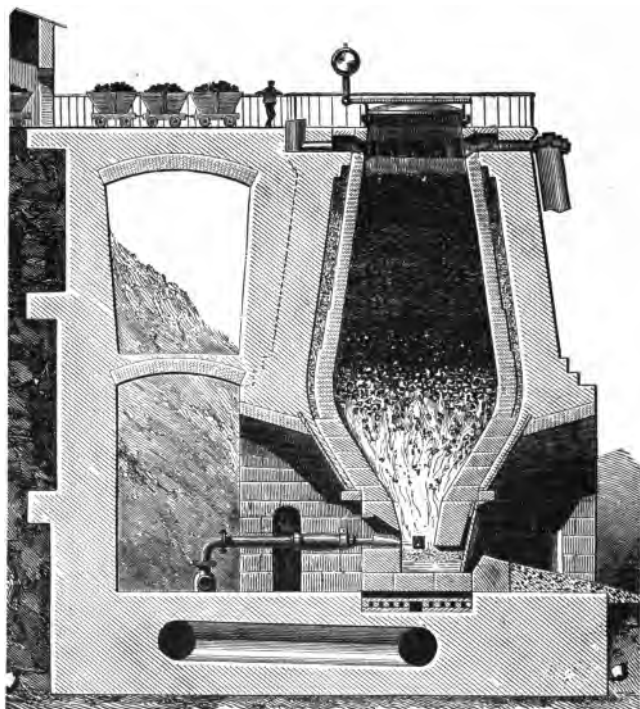


FIG. 51

Operation of the Furnace.—The charge consists of treated ore (which must be converted into oxide by roasting if it is not a natural oxide), coke, and limestone, (CaCO_3). This charge is heated in the furnace until reduction is effected and the molten metallic iron collects in the hearth of the furnace. As reduction takes place the mass sinks into the furnace and is replaced by a fresh charge, the ore, coke, and

limestone being introduced in alternate layers. When the hearth fills up, the furnace is tapped and the cast-iron runs out into troughs molded in the sand. These ingots are *pigs*. Hence the term pig-iron.

The chemistry of the blast furnace is very interesting. At the lower part of the furnace, where the temperature is greatest, the burning coal produces carbon dioxide; at the middle of the furnace the dioxide is reduced to the monoxide by the incandescent coal. In the upper or cooler portion of the furnace the monoxide reduces the oxide of iron, forming a mass of spongy, metallic iron, as the temperature in this part of the furnace is not sufficient to melt the iron; but as the latter passes down to the hotter portion it combines with a part of the carbon and becomes quite fusible. In the hottest part of the furnace some of the silica is reduced to silicon, which combines with the carbon and iron to form a still more fusible substance known as cast-iron. All of the phosphorus and nearly all the sulphur and arsenic go into the pig-iron, imparting certain properties to the latter, mostly of an undesirable kind. If the ore contains manganese oxides, then a part of the manganese will also enter the pig.

Since about 1900 the *electrothermic reduction of iron ores* has been making rapid progress, due to the fact that very high and even temperatures can be obtained. The contamination of the iron with phosphorus and sulphur so frequently contained in the fuels is also eliminated. Ores containing titanium can also be smelted in the electric furnace, whereas the blast furnace will not develop sufficient heat to melt these refractory ores. The Héroult and the Keller are the two types of successful furnaces used in this method of reduction. The chemical reactions taking place within the electric furnace are the same as those occurring in the blast furnace.

Properties.—Iron is a white metal having a specific gravity ranging from 7.7 to 8.1. The pure metal melts at about 1804° C. It is one of the most ductile of metals and is only exceeded in hardness by cobalt and nickel. In the finely divided state iron burns readily in air when heated, and the

iron obtained by reducing with hydrogen may ignite spontaneously upon exposure to air. Upon heating, pure iron becomes soft at red heat and as the temperature rises, it becomes pasty and may be welded at white heat. Pure iron is not acted upon by dry air but in the presence of moisture, and especially carbon dioxide, it becomes coated with rust, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and the process which is slow at the beginning, proceeds rapidly after a film of oxide has been first formed. Iron decomposes water at red heat.

Solubilities.—Iron dissolves in hydrochloric acid and in dilute sulphuric. Concentrated cold sulphuric acid has no action, but the hot acid readily attacks iron.

Dilute nitric acid attacks iron, but the concentrated acid, does not dissolve it. If iron is treated with concentrated nitric acid, the metal is said to become "passive," and the dilute acid will not attack it, nor will it precipitate metals like copper from solution.

Finely divided iron possesses the property of combining with certain gases, carbon monoxide forming iron carbonyl, $\text{Fe}(\text{CO})_5$, and when heated with ammonia, iron nitride, Fe_4N_2 .

Metallic iron precipitates the free metals from solutions of gold, platinum, silver, mercury, bismuth, and copper.

Compounds.—Iron forms three oxides: ferrous, FeO ; ferric, Fe_2O_3 ; and ferrous-ferric, Fe_3O_4 .

Ferric oxide unites with other metallic oxides, forming compounds known as ferrites. $\text{Fe}_2\text{O}_3 \cdot \text{FeO}$ would represent iron ferrite; $\text{Fe}_2\text{O}_3 \cdot \text{CaO}$, calcium ferrite.

Ferrous oxide, FeO , is formed when iron oxalate is heated; it is a black powder and very unstable, rapidly oxidizing to the higher oxides of iron.

Ferric oxide, obtained by heating ferrous sulphate and by quite a few other reactions, is a natural occurring compound of iron.

Ferrosoferric oxide, Fe_3O_4 , occurs as magnetite or lodestone. When iron is heated in air, this oxide is formed; it is also formed when steam is passed over heated iron.

Ferric Hydroxide.—There are several forms of this compound; one form, prepared by treating a ferric salt with an

alkaline hydroxide; if this voluminous, brown, gelatinous precipitate be treated with ferric chloride it dissolves, and upon dialyzing this solution a thick brown liquid is obtained, known as "dialyzed iron."

Iron forms two classes of compounds: ferrous, in which it has a valency of two; and ferric, with a valency of three. The ferrous compounds are unstable and oxidize to the ferric condition.

Potassium ferricyanide, $K_3Fe(CN)_6$, gives a blue precipitate with iron in the ferrous condition; this is known as "Turnbull's blue."

Potassium ferrocyanide, $K_4Fe(CN)_6$, produces a blue precipitate, Prussian blue, with ferric salts.

Potassium sulphocyanate, $KSCN$, produces a red solution with iron in the ferric condition. This is an extremely delicate reaction, showing the presence of ferric iron 1 part in 1,600,000 parts of water.

Iron as obtained from the blast furnace contains impurities; it is called pig-iron or cast-iron.

Cast-iron.—Cast-iron is more fusible and brittle than the other forms of iron. It exists in various forms, depending upon the impurities present and also the manner in which the cast-iron has been cooled.

Cast-iron is classified in two ways:

1. According to composition.
2. According to fracture.

According to Composition.—Cast-iron in the broadest sense is divided into Bessemer and non-Bessemer. Bessemer cast-iron contains 0.1 per cent. or less of phosphorus; the phosphorus is the limiting agent, although the other elements, such as sulphur, manganese and silica are also of some importance.

The non-Bessemer are classed as foundry, basic, mill and malleable irons.

According to Fracture.—This method of classification is not used at the present time to the extent it formerly was. The pig-iron was dropped upon a wedge-shaped piece of iron and examined as to the appearance of the fractured surface.

The appearance of the fracture depended upon the condition of the carbon. The condition of the carbon is dependent upon the temperature of casting, the rate of cooling and the silicon content. A change in any of these factors alters the nature of the fracture. No. 1 iron is dark gray and its grain has large and uniform crystals of graphite to the extreme edge. No. 2 has smaller crystals and a little lighter color. No. 3 is close-grained and lighter in color than No. 2. Mill iron shows no grain and the fracture is a dull shade of gray, the color depending upon the amount of silicon present. White iron, in which nearly all of the carbon is in the combined condition, has no market value and is usually resmelted.

Other alloys formed in the blast furnace are ferrosilicon, silicospiegel, ferromanganese, spiegeleisen and ferrophosphorus. They are of importance in the manufacture of steel.

Wrought Iron.—Wrought iron contains from 0.15 to 0.3 per cent. of carbon, and under these circumstances has a fibrous texture, is very malleable, and its melting point is greatly raised (about 1600° C.). At very high white heat wrought iron becomes liquid, but cannot be cast; there is not sufficient fluidity. An addition of 0.5 per cent. of aluminum lowers the melting point sufficiently to make castings (ornamental iron work, imitation forgings). When the percentage of carbon rises above 0.5 it loses its fibrous texture and becomes granular. "Red short" and "cold short" are terms applied to wrought iron, meaning that it is weak and brittle in either the hot or cold state. Red shortness is produced by the presence of sulphur; cold shortness, by phosphorus. Wrought iron is made by the *puddling process*.

Puddling Process.—The furnace (Figs. 52 and 53) consists of a hearth, *h*, at each end of which there is a fire-brick wall; *b*, the fire-bridge, and *d*, the flue-bridge. The fire grate is at *r*. The hearth is lined with tap cinder and then a coating one and a half inches thick of ferric oxide (fettling).

Operation of Furnace.—The cast-iron is placed into the furnace melted; then well mixed with fettling, (Fe_3O_4). The oxygen of the fettling and of the air removes a large per-

centage of carbon from the iron, with the formation of carbon monoxide. The escape of this gas gives to the mass the appearance of *boiling*. When the reaction ceases the

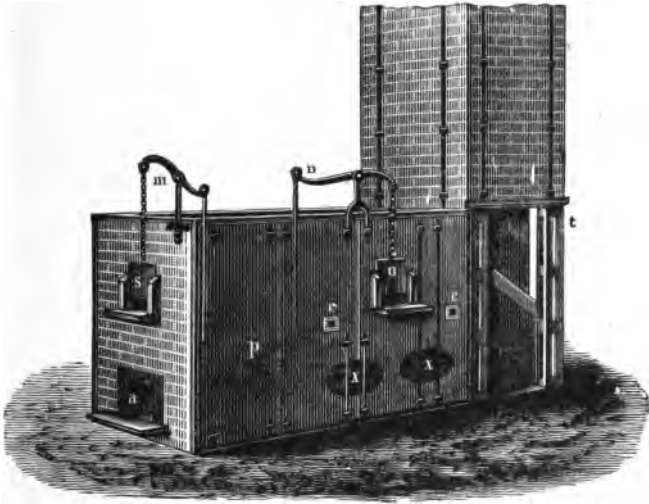


FIG. 52

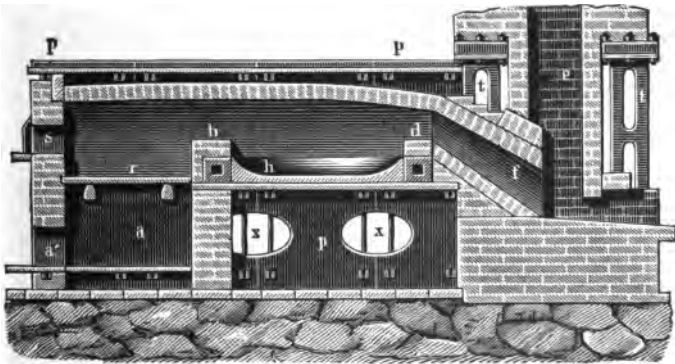


FIG. 53

boiling also stops and the iron is removed from the furnace and put under the hammer to squeeze out the slag and also to condense the porous iron. This operation requires about two hours.

Steel.—This term embraces the varieties of iron which lie between cast-iron and wrought iron.

Steel proper contains only carbon and iron, the former's percentage being between 0.4 and 1.5. The production of hardness is a direct function of the carbon. All other negative elements must be removed down to traces, in order to bring out to the fullest the valuable properties of steel. With 0.4 per cent. carbon the steel is called *soft*; with 1.5 per cent. carbon it is called *hard steel*.

The most valuable property is that the carbon can be made to change its molecular nature; so that even the hardest steel can become soft. This property is called the temper. Low-carbon steel has little temper, while the high-carbon steel has the most. The two conditions of the carbon are called (a) *temper carbon*, making steel hard; (b) *carbide carbon*, making it soft. When a piece of steel is heated to redness and then allowed to cool slowly (annealed), the carbon all becomes carbide variety, the steel is soft. But if the red-hot steel is plunged into cold water, the temper variety is produced, the steel is hardest. This procedure is called tempering. Steel is not as fusible as cast-iron, but more fusible than wrought iron, and can be cast as well as welded.

There are several processes by which steel may be produced, the principal ones being the cementation process, crucible process, and Bessemer process.

Cementation Process.—Bars of wrought iron embedded in charcoal powder in a suitable chest or converting pot (Figs. 54 and 55) made of some substance capable of resisting fire are, after from seven to ten days' exposure to heat, converted into steel, the iron taking up the requisite amount of carbon. The product of this operation is called blistered steel, and is far from uniform, either in composition or texture, as portions of the bars thus produced will be found to contain more carbon than others and the interior to be more or less

porous. For the purpose of improving its quality, the bars are cut into short lengths, made up into bundles, heated to the welding point, and placed under a powerful tilt hammer,



FIG. 54



FIG. 55

which consolidates each bundle into one mass. This is called shear steel.

Crucible Process.—Fusing and casting steel is another process for the treatment of the blistered form, by which is produced the best and most homogeneous variety. It consists in fusing about thirty pounds of broken fragments of blistered steel in a plumbago crucible, the surface being protected from oxidation by glass melted upon it. When perfectly fluid the steel is cast into ingots, and when it is desirable to form a very large ingot several crucibles are simultaneously emptied into the same mold. Cast-steel is superior in density and hardness to shear steel, and is the form best adapted to the manufacture of fine cutting instruments. It is, however, somewhat brittle at red heat, and much care and skill are required in forging it. The addition to it, while fused, of one part of a mixture of charcoal and oxide of manganese affords a fine-grained steel, which may be cast into a bar of wrought iron in the ingot mold, in order that the tenacity of the iron may be an offset to the brittleness of the steel when forged together, while it affords an economical compound in the manufacture of cutting implements, the iron forming the back and the steel the edge of the instrument.

Electrothermic Process.—Hérault has also invented an electric furnace for steel making. The charge may be either all pig-iron, or part pig-iron and part steel scrap, which is melted upon the hearth of the furnace, or the pig-iron can be melted first and then poured upon the hearth. The operations of treating and refining are similar to those of the basic open hearth furnace, except that the heat is produced by electricity instead of gas. The advantages of the Hérault furnace over the open hearth are that any desired temperature can be obtained and therefore a greater variety of slags and fluxes can be used, facilitating the removal of certain impurities. The contamination of the steel with impurities from fuel combustion are also avoided.

Other furnaces (Kjellin, Colby and Gin) for accomplishing the same result, but embodying different principles, have also been constructed.

Bessemer Process.—Bessemer steel is produced by forcing atmospheric air into melted cast-iron which is free from phosphorus and sulphur. The oxygen first takes hold of the silicon, burning it to SiO_2 ; then it burns the carbon, which is oxidized more readily than the iron, forming carbon monoxide, combustion of which takes place on coming in contact with atmospheric air, and sufficient heat is thus generated to keep the temperature above the melting point of steel during the operation. The current of air is stopped as soon as the decarburation has been completed, when a quantity of white pig-iron containing manganese (ferromanganese or spiegel-eisen) is added to the fluid metal for the purpose of assisting the separation of gas from the melted metal and to impart the requisite amount of carbon. It is then ready for casting.

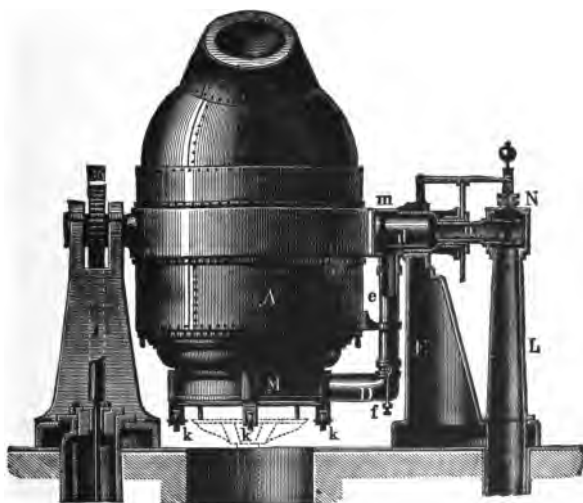


FIG. 56

This process is carried out in the so-called Bessemer converter (Fig. 56), which is an egg-shaped vessel made of wrought iron and lined with gannister, which is an infusible, silicious rock. The bottom of the converter forms the tuyère

box through which the air blast enters the converter. If the iron contains phosphorus it must be treated in one of two ways:

(a) Acid Bessemer process, if the pig-iron contains only traces of phosphorus. The converter is lined with brick made from pulverized quartz (hence acid). Special ores, so-called Bessemer ores, are used in this method.

(b) Basic Bessemer process is used if the pig-iron contains *much* phosphorus, up to 3 per cent., but is low in silicon. Such pig can be made from cheaper ore. The vessel is lined with brick made from magnesite, (MgCO_3), under high pressure.

Hardening and Tempering.—Four kinds of hardness in steel must be recognized, viz.: non-crystal hardness; crystal hardness; refractory hardness of alloy steel; density hardness produced by hammering.

Non-crystal hardness is produced by heating the metal and suddenly chilling it in water, wrought iron absorbing about 1 per cent. of carbon and combining with it, forming an iron carbide (austentite). This carbide is very unstable. Overheating causes the mass to crystallize, and thus degenerate. Reheating the hardened steel to almost 500° F. causes the ferrite (iron) to be set free.

Crystal hardness is usually caused by overheating to the point where the grain previously made dense by hammering or rolling is again opened, thus enlarging the artificially fine crystals. The finer the steel the greater will be the loss of hardness and strength through crystallization.

Refractory hardness is produced in steel by alloying it with some refractory metal which only melts at some extraordinarily high temperature and part of which property the steel acquires, not only chemically, but also physically.

Hardening of ordinary carbon steel is effected by subjecting the object to extremes of temperature. The common practice is to first coat the surface of the metal with some carbonaceous substance, such as soap, to prevent scaling and oxidation of the surface. Ferrocyanide of potassium has also been used for surface hardening. This salt contains cyanogen, (CN),

a gas consisting of twelve parts by weight of carbon and fourteen of nitrogen. This is decomposed at the high temperature which is employed, and supplies carbon to the surface of the metal. This salt is, however, better suited to the process known as case-hardening, while in retempering dental instruments soap answers every requirement.

The metal is next heated to the point of full redness, and then suddenly plunged into cold water, oil, tallow, or mercury, or, in the case of small objects, is merely placed on a large piece of cold metal. It is thus rendered very hard, while at the same time it increases slightly in volume.

If hardened steel be heated to redness and allowed to cool slowly it is again converted into soft steel, but it may be proportionately reduced by heating to a temperature short of redness, the proper point of which may be ascertained by noting certain colors which appear on the ground or brightened surface of a steel instrument when held over a flame. This discoloration is due to the formation of a thin film of oxide, and as the temperature rises the film becomes thicker and darker and the instrument softer. It is therefore necessary to plunge the instrument into a cold menstuum the instant the color indicating the desired degree of hardness is reached. The following table indicates the tempering heats of various instruments:

Temperature.	Color.	Use.
217° to 232° C.	Light yellow.	Enamel chisels.
243° C.	Medium yellow.	Excavators.
258° C.	Brown yellow.	Pluggers.
266° C.	Brown purple.	Saws, etc.
271° C.	Purple.	Wood-cutting tools.
277° to 299° C.	Blue.	When elasticity is desired.

A molten alloy of tin and lead in varying proportions can also be used to supply a uniform heat.

In "letting down" or tempering dental instruments the flame of a spirit lamp may be employed, the instrument being placed in it; the flame should strike, however, some distance from the cutting end, and when the proper color reaches the end it should be thrust into water. Another very convenient means of effecting the same result consists in heating an iron

bar to redness at one end and then fixing it in a vise. The object to be tempered is placed in contact with this until the desired tint appears.

Steel when fractured shows a fine silky appearance of the broken surface. Overheating, however, deprives it of carbon, when the fractured surface presents a coarse, granular condition, showing that it is unfit for use for fine cutting instruments.

A steel instrument may be readily distinguished from one of iron by placing a drop of nitric acid upon it, a dark stain being produced upon steel by the separation of the carbon.

ALLOYS OF STEEL.—By alloys of steel are meant those steels that owe their special properties to the presence of other elements other than carbon.

Copper Steel.—The alloys of copper and steel are noted for their property to resist the action of corrosion. A product recently placed upon the market known as “Vismara,” is said to be highly resistant to the action of agents which ordinarily corrode steel. This alloy contains about 0.2 per cent. of copper. Higher alloys containing from 5 to 20 per cent. of copper are said to possess great strength, tenacity and malleability.

Harveyized Steel.—Harveyized steel is steel heated to about the melting point of cast-iron and then the surface of the metal treated with carbon. The carbon percentage in the steel is raised about 1 per cent., and then plunged into water and cooled. The surface of the steel so treated is extremely hard and resistant and is used for armor plate.

Aluminum Steel.—The addition of aluminum slightly increases the tensile strength and proportionately the elasticity, in rolled and cast-steel when the amount added is not greater than 1 per cent.

Aluminum is also added to molten steel, especially when the mass has been chilled so that it will not pour readily; the aluminum reduces the fusing point of the steel and thus assists in the pouring.

Chrome Steel.—Chrome steel contains from 1.5 to 2 per cent. of chromium, generally added as ferrochrome. This

steel possesses hardness and tensile strength, but interferes with the welding. It is used sometimes for tools but mainly for giving very hard surfaces and resistance to severe shocks.

Nickel Steel.—This steel usually contains from 5 to 30 per cent. nickel. This is a very useful alloy of steel because of the physical properties which it possesses. It is said to increase the strength of steel about 50 per cent., less liable to corrode; besides these properties it also adds to the life of the alloy, as it has about six times the resistance to fatigue.

The presence of small quantities of manganese in nickel steel is most important, as it appears that without the aid of manganese in proper proportions the best results could not be obtained.

This steel works readily hot or cold, forges easily, and machines harder than carbon steel.

Manganese Steel.—Depending upon the quantity of manganese present the physical properties of this steel are brittle or extremely tough. With a low content of manganese, say 1.25 per cent., a very brittle unworkable product is formed; however, an alloy containing from 7 to 14 per cent. is very peculiar. It possesses extreme hardness and toughness. It is so hard that castings made from it are not touched by the file, yet it may be hammered like the softest of mild steels. It possesses non-magnetic properties and is used on this account in the construction of dynamos.

Tungsten (Musket Steel).—Tungsten steel is produced by alloying a certain percentage of tungsten with steel. If from 3 to 3.5 per cent. of metallic tungsten is melted together with low-carbon steel, an alloy results which does not need tempering; it turns hard even on slow cooling (air-quenched steel). It is sometimes quenched by blowing a blast of air, which gives it greater hardness than if allowed to cool in quiet air. If the alloy be plunged in oil or water to quench it, it becomes so hard that the strain overcomes the cohesion of the molecules and cracking results. This alloy is used as a so-called "high-speed tool steel." It can be used in lathes and boring mills, and the heat produced in no way affects the temper of the steel, thus causing a great saving of time.

Vanadium Steel.—Carbon steel or alloy steels generally contain from 0.1 to 1 per cent. of vanadium. It is claimed that this element acts by removing dissolved gases, especially nitrogen, with the result that the greater part of vanadium is eliminated in the slag. However, the vanadium remaining in the steel greatly modifies its microscopic appearance.

Vanadium has little virtue if used alone, but when combined with other elements acts very beneficially.

High-speed Steels.—High-speed steels so-called on account of the great rapidity with which they machine metals. They usually contain under 1 per cent. carbon, from 12 to 24 per cent. tungsten, and 0.3 per cent. manganese. Sometimes the tungsten is replaced by 10 per cent. of molybdenum. These steels will retain their toughness and hardness at a red heat, and therefore tools made from them can be run at such a high rate of speed that they will become red hot from friction. High-speed steel is tempered by heating to about 1100° C., and cooling by blowing a blast of cold air upon it.

RESUMÉ.

Symbol, Fe.	Tenacity, 1st.
Valency, II or III.	Specific gravity, 7.7 to 8.1.
Atomic weight, 55.84.	Crystalline form, isometric.
Melting point {	Chief ore, hematite.
	Conductivity of heat, 120.
	Conductivity of electricity, 17.5.
Specific heat, 0.1138.	Coefficient of expansion, 0.000012.
Boiling point, 2450° C.	Ductility, 4th.
Malleability, 9th.	
Color, bluish.	

CHAPTER XIX.

ALUMINUM.

Symbol, Al. Atomic weight, 27.1.

Occurrence.—Aluminum of all the metals, occurs in the greatest abundance. The native metal is not found in nature. In the combined condition it is present in many silicates and is an essential constituent of all clays.

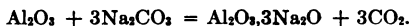
The aluminum minerals may be classed: (1) Ores of aluminum, (2) abrasive materials, (3) gems.

Ores of aluminum, bauxite, $\text{Al}_2\text{O}(\text{OH})_4$, gibbsite, $\text{Al}(\text{OH})_3$, are the principal ores of aluminum.

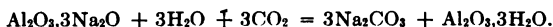
Abrasive materials, corundum, Al_2O_3 . This substance ranks next to the diamond in the scale of hardness. *Emery* has the same composition with a small amount of oxide of iron as impurities. These materials were used extensively as abrasives until the introduction of carborundum, which is an artificially prepared carbide of silicon, SiC . Cryolite, Na_3AlF_6 , the sodium aluminum fluoride is of importance in the reduction of aluminum.

Reduction.—Before the introduction of the electrolytic process most of the aluminum was prepared by the following method:

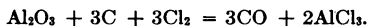
Bauxite is first freed from iron: 1. The powdered bauxite is mixed with sodium carbonate and heated in a reverberatory furnace.



2. The sodium aluminate is extracted with water, leaving the iron as an insoluble oxide. Carbon dioxide is passed through the filtered solution, decomposing the sodium aluminate.



3. The purified oxide of aluminum is dried and mixed with sodium chloride and powdered wood charcoal. Water is then added to the mass which is then worked up into balls. These are dried at 150° and then packed into a fire-clay cylinder and strongly heated in a stream of chlorine:



The aluminum chloride combines with sodium chloride and volatilizes from the retort. It is collected in earthenware receivers and represents the aluminum entirely freed from iron.

4. The double chlorides are then reduced by metallic sodium. The charge is introduced into a heated reverberatory furnace and a violent reaction occurs; after a short time metallic aluminum separates out beneath the slag and is collected. Cryolite is used as a flux in this reaction.



The chemical processes are now largely replaced by the electrolytic ones.

The Hérault and the Cowles processes both depend upon electrolysis, but they only are adapted to the making of aluminum bronzes. Although antedating the Hall method, they cannot be used for making pure aluminum.

The Hall Process.—In this process advantage is taken of the solvent action of cryolite for bauxite. This solution conducts an electric current and the cryolite is not decomposed, with the result that aluminum is freed from its combination with oxygen.

The other solvents for bauxite which were used in the past would be decomposed by the current before the oxide of aluminum would be attacked. The vessels or pots employed in this process are rectangular iron boxes, thickly lined with carbon. The carbon lining constitutes the cathode. The anodes consist of carbon cylinders, and are supported above the pots, dipping into the bath of fused fluorides. No external heat is employed, the heat developed by the resistance to the current being all that is necessary to maintain fusion.

Aluminum is added from time to time as required. The process proceeds quietly, the resistance offered by the bath charged with alumina being very low, but the moment the alumina is exhausted the resistance increases fourfold. In order that the workmen may be made aware of the state of the bath, an incandescent lamp is attached to each bath, which emits no light during the low resistance, but shines brightly when the resistance and consequently the electromotive force at each bath increases sufficiently; so whenever one of the incandescent lamps begin to shine the workmen hasten to stir in a fresh supply of alumina. The process proceeds quietly day and night. It is only necessary to keep the baths supplied with alumina, and every twenty-four hours tap the pots and draw off the metal. There are over one hundred of these pots altogether, and the yield is about one hundred pounds of aluminum per pot every twenty-four hours, or about ten thousand pounds altogether.

Properties.—Aluminum is a white metal, odorless and tasteless, very ductile and malleable. It is about as hard as silver. The specific gravity of aluminum is about 2.56 and it is the lightest of the metals in common use.

Commercial aluminum is never pure and a product purer than 99.75 per cent. is rarely obtained even in purified varieties: generally containing silica, iron and sometimes lead or copper. It crystallizes in octohedrons. It fuses at 654° C., and requires an extremely high temperature to volatilize, about 1800°. Like zinc, aluminum is best rolled between 100° and 150°. It may be rolled or hammered out into foil and is also obtained in the powdered form.

Powdered aluminum possesses a great affinity for oxygen, taking the oxygen from combination with other metals and liberating an intense heat. It possesses the property of sonorousness to a remarkable extent, more so than any other metal.

Aluminum is unaltered by the air, even in the presence of moisture. When heated in thin sheets in a current of oxygen it burns and is converted into the oxide. It conducts an electric current about one-half as well as copper and conducts

heat about two-thirds as well as silver. When molten it possesses great fluidity but because of its lightness is rather hard to cast by simply pouring. For commercial purposes zinc is added to aluminum to aid in the casting process.

Aluminum is used in the construction of dental bases for artificial dentures, and depending upon the method of construction there are two varieties of aluminum bases: (a) cast; (b) swaged.

Cast Aluminum Bases.—The objections to aluminum in this class of work are: (1) warpage; (2) lack of density of the cast aluminum; (3) reaction of the fluid of the mouth upon the metal. Warpage results from two causes, *i. e.*, changes in the investment and also contraction of the aluminum during solidification and cooling. Dr. H. J. Goslee, in an article published in the *Dental Review*, August, 1914, suggests an indirect method of casting. The object of this method of casting is to correct any warpage by a subsequent swaging. Richards states that to overcome the difficulties of contraction and corrosion by the fluids of the mouth Dr. Carroll adds a little copper, which, he says, decreases the contraction while the addition of some platinum and gold renders it unalterable in the mouth.

Cast aluminum, under the microscope appears irregular upon its surface, and the presence of organic acid or alkalies may find points of lodgment in these irregularities, causing a dissolution of the aluminum. For this reason cast aluminum is not as resistant to the fluids of the mouth as it should be.

As aluminum was used in the past the metal was supposed to contain sufficient quantities of iron, as a result of this a voltaic couple was formed, causing a solution of the aluminum. Dentures were frequently seen in which small holes had been found completely penetrating the denture.

Aluminum is generally annealed by coating its surface with sweet oil or vaseline and then igniting; when the last trace of carbon burns from the surface the metal is quickly plunged into water. If the metal be held in the free flame it frequently happens that a portion of it will fuse.

In melting small chips of aluminum or those of its light

alloys only about 30 per cent. of the metal melts. It was discovered that by adding small quantities of anhydrous aluminum chloride, AlCl_3 , 50 to 60 per cent. was melted. By two or three operations of this kind a 70 per cent. melt is possible.

Swaged aluminum dentures are supposed to possess greater density due to the mechanical treatment to which the aluminum has been put to. There is a difference of opinion as to which form of aluminum denture possesses the greatest lasting powers. Prothero points out the fact that 26-gauge aluminum, which is the form mostly used in this work, is only about one-third the thickness of the average cast-plate, consequently the age of a cast-plate should exceed that of a swaged one.

For some time the difficulty of soldering aluminum prevented the metal from being applied to useful purposes. The solder recommended for general use in the manufacture of articles of ornamentation is composed of copper, four parts; aluminum, six parts; zinc, ninety parts. The use of this requires some skill and experience. At the moment of fusion small aluminum tools are used, the friction of which is necessary to induce adhesion. Borax cannot be employed as a flux, as it is liable to attack the metal and prevent union.

Another method of uniting two pieces of aluminum with ordinary solder in conjunction with silver chloride as a flux has recently been recommended by F. J. Page and H. A. Anderson, of Waterbury, Conn. The finely powdered fused silver chloride is spread along the lines of junction, and the solder is melted with a blow-pipe or other device. The union thus obtained is said to be perfectly strong and reliable.¹

The following alloys are also used as solders in unalloyed aluminum articles of jewelry:

	I.	II.	III.	IV.
Zinc	80	85	88	92
Aluminum	20	15	12	8

In soldering with these alloys a mixture is used as a flux consisting of three parts of copaiba balsam, one part of

¹ Chemical News, iv, 81.

Venetian turpentine, and a few drops of lemon juice. The soldering iron is dipped into the mixture.

Mr. William Frismuth, of Philadelphia, recommends the following solders for aluminum, with vaselin as the flux:

SOFT SOLDER.

Pure block tin	from 90 to 99 parts
Bismuth	from 1 to 10 parts

HARD SOLDER.

Pure block tin	from 90 to 98 parts
Bismuth	" 1 to 5 "
Aluminum	" 1 to 5 "

Schlosser¹ recommends two solders containing aluminum as especially suitable for dental laboratory use:

PLATINUM-ALUMINUM SOLDER.

Gold	30 parts
Platinum	1 part
Silver	20 parts
Aluminum	100 "

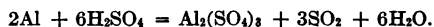
GOLD-ALUMINUM SOLDER.

Gold	50 parts
Silver	10 "
Copper	10 "
Aluminum	20 "

Solubilities.—The best solvent for aluminum is hydrochloric acid.



When heated with strong sulphuric acid aluminum dissolves with the liberation of sulphur dioxide:



Nitric acid, dilute or concentrated, does not attack aluminum. Organic acids in the presence of sodium chloride attack aluminum.

A 4 per cent. solution of acetic acid even in the presence of

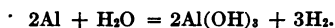
¹ Richards.

sodium chloride has very little action on this metal and when the above mixture was heated for fourteen hours, only one part of aluminum in five hundred and twenty-six parts of the acid was found.

Sodium and potassium hydroxides attack aluminum with the formation of aluminates and hydrogen.

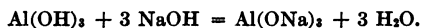


Powdered or leaf aluminum when boiled with water decomposes it with the evolution of hydrogen.



Compounds.—Oxide, Al_2O_3 , occurs native in a colorless crystalline condition as corundum, and colored by traces of various metallic oxides in the precious stones such as *ruby*, *sapphire*, and *amethyst*. In less pure conditions it occurs in large quantities as emery. It may be prepared in an amorphous condition by igniting the hydroxide, nitrate, and various other salts of aluminum.

Aluminum hydroxide, $\text{Al}(\text{OH})_3$, is prepared by treating a solution of an aluminum salt with ammonium hydroxide. Aluminum hydroxide is capable of acting as a feeble acid oxide; thus, the hydroxide is dissolved by sodium or potassium hydroxide with the formation of aluminates.



Alloys.—When mercury comes in contact with a polished aluminum surface, the surface immediately becomes dull, and a moss-like growth of aluminum hydroxide arises upon the surface. The aluminum amalgam first formed is decomposed because the aluminum in the amalgam is attacked by the oxygen of the air.

E. Kohn states that aluminum amalgam may be prepared by dipping aluminum into a solution of mercuric chloride; this amalgam oxidizes with the evolution of hydrogen from the solution.

It has been suggested that this amalgam may be used to free water from coloring matter as it precipitates tannates

from solution. Copper present to the extent of 0.1 per cent. is said to prevent the decomposition of this amalgam.

Aluminum Bronze.—Aluminum and copper readily alloy, and alloys containing up to 15 per cent. of aluminum possess hardness, do not tarnish and possess increased tensile strength. The color closely resembles gold, and it is sometimes used for souvenir metals.

The following solders are well adapted to aluminum bronze:

I. HARD SOLDER FOR 10 PER CENT. ALUMINUM BRONZE.

Gold	88.88	per cent.
Silver	4.68	"
Copper	6.44	"
	<hr/>	
	100.00	"

II. MEDIUM HARD SOLDER FOR 10 PER CENT. ALUMINUM BRONZE.

Gold	54.40	per cent.
Silver	27.00	"
Copper	18.00	"
	<hr/>	
	100.00	"

III. SOFT SOLDER FOR ALUMINUM BRONZE.

Copper 70 per cent.	} Brass	14.30 per cent.
Tin 30 "		
Gold		14.30 "
Silver		57.10 "
Copper		14.30 "
		<hr/>
		100.00 "

For a flux: "Gaudin's liquid flux" consisting of pulverized cryolite and phosphoric acid dissolved in alcohol.

Aluminum and copper: Fenchel states that with a high percentage of gold these alloys are hard and brittle.

Zinc and tin also form brittle alloys with aluminum.

Silver and aluminum form alloys, and in the presence of 4 per cent. silver an alloy is obtained which may be more readily worked with a file than pure aluminum. Petrenko claims a 7 per cent. silver alloy will not tarnish upon exposure to the air.

Nickel forms several compounds with aluminum.

RESUMÉ.

Symbol, Al.	Crystalline form, octa-
Valency, III.	hedrals.
Atomic weight, 27.1.	Chief ores, bauxite.
Melting point, 654.5° C.	Conductivity of heat, 5th.
Specific heat, 0.2143.	Conductivity of electricity,
Boiling point, 1800° C.	63.
Malleability, good.	Ductility, 8th.
Color, white.	Coefficient of expansion,
Specific gravity, 2.56.	0.00002313.
	Tenacity, good.

CHAPTER XX.

ZINC.

Symbol, Zn. Atomic weight, 65.37. Valency, II.

History.—Zinc was known to the ancient Greeks under the name of cadmia and was used in the manufacture of brass. There is no record of the method used by them in reducing zinc ores. Until the eighteenth century the zinc of Europe was imported from China.

So far as can be ascertained this metal was discovered by the moderns. It is said, however, to have been known in China, and is noticed by European writers as early as A.D. 1231, though the method of extraction was not known until five hundred years after. A mine in Yorkshire, England, was discovered in 1809. This date may be considered as the starting point of the modern industry as it is known today. The name zinc was given to the metal by Paracelsus in the sixteenth century.

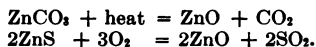
Occurrence.—Missouri, Kansas, Indiana and Illinois, yield most of the zinc ores of the United States; although other important deposits exist in Pennsylvania, New Jersey, and Virginia.

The principal sources of zinc in Europe are located in England, Hungary and Silesia. Zinc, as a rule, does not exist in the free state in nature, although it is claimed that the native metal has been found near Melbourne, Australia.

The principal ores are: sulphide, sphalerite, (ZnS) ; oxide, zincite or red zinc, (ZnO) ; carbonate smithsonite or calamine, (ZnCO_3) ; silicates willimite, $(\text{Zn}_2\text{SiO}_4)$; calamine, $(\text{ZnOH})_2$, SiO_3 ; oxide franklinite or horseflesh ore, $(\text{FeMnZn})_3\text{O}_4$. Zinc carbonate is also known as zinc blend. Blend is derived from the German, meaning to dazzle, which refers

to the brilliancy of the crystals, which are almost black, due to the presence of iron sulphide.

Reduction.—The ore is first roasted in a reverberatory furnace; then distilled, mixed with charcoal, in closed earthen or iron vessels. The roasting converts the carbonate or the sulphide into the oxide:



The charcoal reduces the oxide and the free zinc distils over into the receivers.

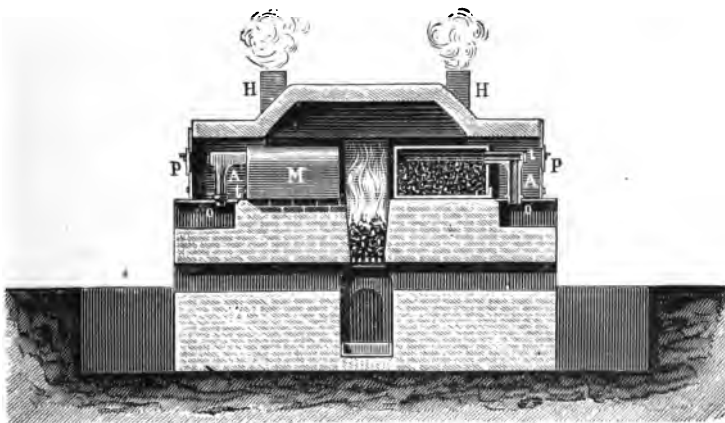


FIG. 57

The process varies in different countries; in Silesia, Germany, fire-clay muffles are used, this is known as the Silesian process (Fig. 57); in Belgium, earthenware tubes, Belgian process (Fig. 58); and in England, fire-clay retorts. The English furnace is conical in shape, having an interior dome; six crucibles are placed within the furnace, each has a hole in the bottom, through which an iron pipe passes to convey the zinc vapor. After placing the charge of zinc oxide

and coke in the crucible, the top is cemented into place and the crucibles are heated until a bright red heat is obtained.

The first portions of the gas from the iron tubes are commonly very impure, containing cadmium and arsenic and the

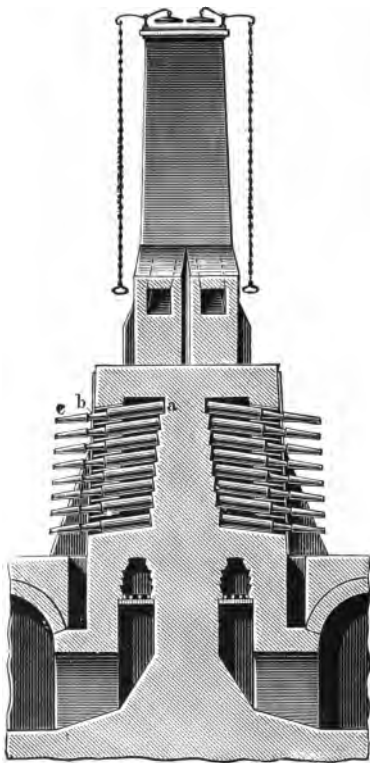


FIG. 58

gases burn with the so-called "brown blaze;" but when the "blue blaze" begins, that is, when the metallic vapor burns with a bluish-white flame, the zinc is collected in suitable vessels placed beneath. The reduced zinc is afterward cast into ingots; this product is impure zinc, known as

spelter, and contains generally iron, cadmium, lead, copper, carbon and arsenic as impurities.

Physical Properties.—Zinc is highly crystalline in nature, having a brilliant lamellar crystalline structure upon fracture. It does not tarnish in dry air and is only slowly acted upon even in moist air with the superficial formation of the carbonate.

Specific gravity, 6.861 (cast) to 7.142 of the rolled varieties.

Melting point, 415° C., 779° F., below red heat.

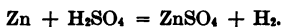
Boiling point, variously stated from 916° to 1040° C., or 1681° to 1742° F. When heated to a bright red heat with excess of air, zinc burns with a bluish-white flame with the formation of a white flocculent substance, ZnO, resembling wool and formerly known as philosopher's wool. At ordinary temperature it breaks with a crystalline fracture, but when heated to a temperature from 100° to 150° C., it becomes malleable and at these temperatures may be rolled into sheets or drawn into wire. Zinc so heated retains its malleability at ordinary temperature. Above 150° or about 205° C., it again becomes brittle, and at a temperature just below its fusing point it is so brittle that it may be pulverized in a mortar. Conductivity of heat, 303; conductivity of electricity, 5.751 or about fourth. It ranks eighth in malleability and sixth in ductility. Zinc is frequently used in the construction of a voltaic cell because of its position in the electromotive series. Zinc precipitates nearly all metals from solution and is itself precipitated by magnesium in an acetic solution. Zinc possesses a rather high degree of expansibility, and is consequently used for the purpose of making dies for swaging metal plates for artificial dentures. By many dentists it was formerly thought that a metal, to be well suited for this purpose, should be entirely destitute of this property, so that after casting the die should not, in returning to its former condition in cooling, be smaller than the plaster model, the object *per se* being to have the plate fit the plaster cast perfectly; whereas, the real purpose should be to make the plate fit the mouth closely, the plaster model being only a means to the end. Plaster expands in setting. From the

impression to the model two expansions are gone through before the *fac-simile* of the mouth in plaster is obtained; hence a plate made to fit such a model perfectly must necessarily be somewhat larger than the mouth—a condition unfavorable to atmospheric adhesion. On the other hand, a plate to fit the zinc will not be found too small for the mouth, but will, provided the impression is a good one and represents perfectly the conformation of the mouth, afford a very close-fitting plate. Even better results might be expected where the plate is somewhat smaller than the mouth, because such a condition would, in entire upper dentures, throw any undue pressure upon the alveolar ridge, while that portion of the plate covering the palatine arch would barely be in contact with the tissues; the pressure along the ridge would quickly promote absorption of the alveoli, and a uniform adaption of the plate to the mouth would soon follow. On the contrary, if the plate be made to fit the plaster cast, and is a trifle larger than the mouth, the pressure will be thrown upon the palatine arch at the back edge of the plate, at a region not likely to change by absorption, as is the case with the alveolar ridge, and hence the margin of the plate will embed itself in the tissues and cause much discomfort and impair the usefulness of the denture.

Much time and thought have been expended in the effort to discover some alloy which, in connection with the properties of hardness and fusibility, shall possess that of non-expansibility when heated. Harris's *Principles and Practices of Dentistry* gives no less than nine different formulæ. The author is satisfied that the property of expansibility in zinc as used in the dental laboratory constitutes one of its most valuable qualities, as it gives us the means of compensating for the yielding of the tissues and the absorption along the ridge which nearly always follows the first insertion of an artificial denture.

Solubilities.—Pure zinc dissolves very slowly in acids or alkalies unless in contact with copper, platinum or some less positive metal. The metallic impurities in ordinary zinc enables it to dissolve easily with acids or alkali hydroxide.

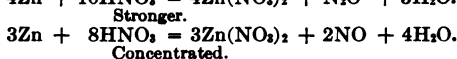
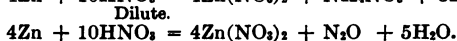
In contact with iron, it is quite rapidly oxidized in water containing air, but not dissolved by water unless by aid of certain salts. It dissolves in dilute hydrochloric, sulphuric and acetic acids.



With aqueous solutions of the alkalies, zincates are formed:



Nitric acid attacks it with the formation of zinc nitrate, and depending upon the strength of the acid, ammonium nitrate, nitrous oxide, or nitric oxide is formed.



When zinc is treated with hot sulphuric acid the following reaction takes place:



Alloys.—*Mercury* forms with zinc an exceedingly brittle amalgam. The two combine in the cold state, but union is greatly facilitated by heating.

Silver.—Zinc is said to form two compounds, Ag_2Zn_3 and AgZn with silver. One per cent. of zinc is often added to silver to prevent oxidation and to avoid the so-called spitting during crystallization. Aluminum and zinc are miscible in all proportions but no chemical compounds are formed.

Platinum.—Combination between zinc and platinum or palladium may be effected at a comparatively low temperature and is accompanied by evolution of light and heat.

Zinc and Lead.—These metals are insoluble in one another and it requires a high temperature to cause them to be miscible at all. If the two metals are melted together and allowed to cool they will separate into two distinct layers, the zinc having the lesser specific gravity will be the top layer and the lead the lower portion. The zinc retains 1.2

per cent. of lead, and the lead 1.6 per cent. of the zinc. The necessity of carefully keeping these two metals separate in all molding operations in the dental laboratory will readily be appreciated, as a failure to preserve precaution in this direction will be followed by vexatious consequences. If by accident lead becomes mixed with zinc used for dies, the lead, by its greater specific gravity, will settle to the bottom and fill up the deeper portions of the sand matrix representing the alveolar ridge, the most prominent part of the die. This may not be discovered until an attempt to swage is made, when the die will be found to be totally unfit for the purpose. In such cases the mixed metal should be discarded and new zinc substituted.

Zinc and Tin.—These are miscible in all proportions in the fluid state but they form no true chemical compound. There is a eutectic having 16 per cent. by weight of zinc and 84 per cent. tin which melts at 190° C.

Alloys of zinc and tin are frequently employed in casting dies for swaging plates. Richardson's formula consists of zinc four parts, tin one part, which he claims fuses at a lower temperature, contracts less on cooling, and has less surface hardness than zinc.

Zinc and Copper.—Copper and zinc are miscible in all proportions, Bornemann claims the existence of the compound Cu_2Zn_3 ; other compounds also are said to be formed corresponding to the formulas CuZn and CuZn_4 .

Brass.—Brass composed of zinc, 27 to 37 per cent., and copper, 63 to 73 per cent., is used in the manufacture of wire and sheet brass.

Mosaic gold, according to Fischer contains 33.3 to 36.7 per cent. zinc, and copper 63.3 to 66.7 per cent. This alloy is so-called because of its color.

German silver is an alloy of copper, zinc, and nickel.

Bell metal contains copper, zinc, and tin.

Galvanized iron is prepared by coating sheet steel with zinc by a dipping process. There is supposed to be an alloy formed between the zinc and the iron which prevents the zinc from separating from the iron. The zinc is not readily acted

upon by the atmosphere and prevents the oxidation of the iron.

Zinc is the metal most commonly employed in the formation of dies for swaging plates. Another important application of zinc is in the formation of counter-dies. The die is placed in the iron ring when a Baily flask is employed, or invested in the molding sand and then surrounded by a suitable iron ring in the old-fashioned way. The zinc is then heated and poured in upon the zinc die just at the moment of complete fusion. Should the metal be accidentally allowed to remain on the fire too long, and thus reach a higher temperature than is necessary, it should not be poured until it begins to solidify at the edges. The belief seems to be pretty general that melted zinc cannot be poured upon a zinc die without causing cohesion, but if the necessary precaution regarding the proper temperature at which the metal is poured is observed it is impossible for union to take place; when cool the die and counter-die will separate quite as readily as though the latter was of lead. It frequently occurs that the zinc die and lead counter-die are totally inadequate to bring a plate (particularly if the latter is of platinum-gold or iridium-platinum) into perfect adaptation to all parts of a model, especially where the palatal arch is very deep and the rugæ are prominent.

The suggestion has been made of coating the zinc with whiting and alcohol mixture in case there is doubt in the operator's mind of the advisability of the above procedure. Zinc counter-dies are not expected to supersede lead counter-dies but to be used in conjunction with them.

Zinc dies or counter-dies should be handled very carefully after pouring. If the die should be dropped while still hot its destruction would result. Zinc will, under favorable conditions unite with iron, and it frequently attacks the cast-iron ladle in which it is melted, and may penetrate the side and escape into the fire. Accidents of this kind may be prevented by coating the inside of the ladle with whiting.

Compounds of Zinc.—Zinc oxide is formed when zinc is burned in air, it may also be prepared by igniting in air, either the hydroxide, carbonate, nitrate, or oxalate.

Zinc oxide for dental purposes should be of a high grade of purity. The presence of arsenic in this compound has given a great amount of trouble in the past in certain dental preparations. Zinc oxide free from arsenic should be prepared from metallic zinc obtained from ore free from arsenic, as arsenic is extremely difficult to separate from zinc and its compounds.

Among the impurities found in commercial zinc oxide may be enumerated the following: arsenic, sulphates, chlorides, nitrates, and the carbonates of calcium, magnesium and foreign metals.

To test zinc oxide for arsenic the following may be used: A mixture of 1 gram of zinc oxide and 3 c.c. of stannous chloride solution should not acquire a darker color on standing one hour. (Indicating less than 0.0015 per cent. arsenic.)

Zinc oxide is used in the preparation of dental rubber for vulcanite purposes; in the preparation of temporary stopping, and finally in dental cements. Zinc oxide is a pure white substance which, when heated, turns yellow but again becomes white on cooling; when strongly heated in oxygen it may be obtained in the form of hexagonal crystals; such crystals are occasionally found in the cooler parts of zinc furnaces. The oxide does not fuse in the oxyhydrogen flame, but like lime, under these circumstances it becomes intensely incandescent.

Dental Cements.—Oxychloride cements consists of a liquid prepared by dissolving zinc chloride in water and a powder of zinc oxide.

Oxyphosphate.—The liquid consists of orthophosphoric acid, H_3PO_4 , modified with some suitable phosphate. The so-called hydraulic cements, *i. e.*, those which possess the property of setting in the presence of moisture, generally contain a phosphate of a metal other than the alkali metals, such as zinc phosphate or aluminum phosphate. The non-hydraulic cement liquids contain sodium or other alkali metals as a modifying agent. The powder is calcined zinc oxide together with coloring agents. There are a few cements on the market in which the powder contains phosphates; as

a rule these are rather slow-setting cements. The other dental cements should be described in dental chemistry and have no place in metallurgy. The preparation of a dental cement is a very exacting procedure, and demands the knowledge of a specialist in this branch of chemistry. It would be a loss of time, and the writer can see no reason why a dentist should be called upon to prepare his own cements; for this reason I have not given formulas or exact procedures used for the preparation of cements.

Zinc chloride is prepared by the action of hydrochloric acid upon zinc, or by the direct action of chlorine upon metallic zinc. It is a soft, white, easily fusible solid which volatilizes and distills without decomposition. It is extremely deliquescent (absorbs moisture from the atmosphere). From aqueous (watery) solutions, deliquescent crystals are deposited, having the composition $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$.

Besides, as a medicinal agent zinc chloride is also used as a flux in soft soldering. In soldering tinware the surfaces are coated with "cracked muriatic acid," hydrochloric acid in which some zinc has been dissolved. For galvanized ironware hydrochloric acid alone is used; this acid dissolves enough zinc from the metallic surface to form zinc chloride which then acts as a flux.

RESUMÉ.

Symbol, Zn.	Chief ore, carbonate, calamine.
Valency, II.	
Atomic weight, 65.37.	Conductivity of electricity, 27.72.
Melting point, 415°C .	Conductivity of heat, 190.
Specific heat, 0.095.	Coefficient of expansion, 0.0000294+.
Boiling point, 916°C .	Ductility, 6th.
Malleability, 8th.	Tenacity, 6th.
Specific gravity, 6.86 to 7.2.	
Crystalline form, rhombohedral.	

CHAPTER XXI.

NICKEL.

Symbol, Ni. Atomic weight, 58.68.

Occurrence.—Garnierite, a magnesium, nickel silicate is the principal working ore of nickel, $H_2(NiMg)SiO_4 \cdot H_2O$. The other minerals are the sulphides, NiS, millerite and pentlandite, $(Fe, Ni)S$, arsenide, NiAs, niccolite. Nickel is also obtained as the oxide in the working of pyrrhotite, Fe_7S_8 (sometimes called magnetic pyrites), and chalcopyrite, $CuFeS_2$, of Sudbury, Canada.

Native nickel is found with iron in meteorites.

Reduction.—The oxide may be reduced by the “Mond” process. Carbon monoxide is passed over gently heated nickel oxide which is first reduced to metallic nickel and then the excess of carbon monoxide combines with the nickel, forming volatile nickel carbonyl, $Ni(CO)_4$. This compound is passed through tubes more strongly heated which decompose it with the liberation of metallic nickel. In this way the metal is deposited in a coherent mass entirely free from cobalt.

The sulphide ores are reduced by roasting and then smelting with a suitable flux, a nickel matte results which contains iron and copper as impurities, this is run into a silica-lined Bessemer converter and air-blown. A matte, rich in nickel and copper, results. This matte is fused with sodium sulphate and coke. The nickel sulphide is roasted and converted to the oxide. Then upon heating with charcoal to a white heat in a graphite crucible, nickel results. Another process of treating the sulphide briefly described is as follows: Roasting the sulphide, smelting with a suitable flux in a blast furnace forming a matte; air-blowing the fused matte; again roasting which results in the production

of NiO and CuO. Dissolve the oxides in sulphuric acid; the copper precipitated by electrolysis; crystallize nickel sulphate from the solution; obtaining the nickel as NiO by adding milk of lime and drying the precipitate formed. The nickel oxide is reduced by making a mixture of starch and charcoal with the oxide into a paste, forming into cubes and then heating to a white heat in a crucible.

There is also an electrolytic method of reduction, the details of which are a secret.

Properties.—Nickel is a hard white metal having a yellowish tinge by which it may be distinguished from silver. It takes a high polish and is malleable, ductile and very tenacious. In wire form it is stronger than iron but not as strong as cobalt. It is magnetic but loses its magnetism, like steel, when heated to redness. It imparts hardness to its alloys.

It has always been the belief that the primitive people possessed the knowledge of tempering copper; the following item, taken from *The Engineering and Mining Journal*, tends to disprove this statement and also shows the effect that nickel produces on other metals. The copper-cutting instruments of the Tarascans are so hard that they would turn the edge of a modern knife, and it has been claimed, that these people along with the Aztecs and Toltecs, possessed the secret of tempering copper. On the other hand, copper knives and axes found at Alcopotzalco are so soft that they can be cut with a knife. Analysis shows that in all three localities the copper implements were of the same composition as the copper ore found therein.

The blades from Guerrero, which are hard and apparently tempered, were made from the natural ore carrying nickel and cobalt, thus rendering the smelted alloy steel-like in hardness. Thus the natural product gave an alloy of great hardness when heated and sharpened, while the other ores of practically pure copper, when smelted in implements were soft and inferior in cutting value. The sharp-cutting implements were therefore the result of Nature's handiwork, and it is indeed very questionable whether these people possessed the secret of "tempering."

Nickel is not acted upon in dry air or moist air at ordinary temperatures for this reason it is used to coat other metals, such as copper, brass, steel, etc., to prevent corroding and to preserve a bright metallic surface. The coating is given the metals by an electrolytic process. When nickel is heated it burns with incandescence in the presence of oxygen, chlorine, bromine or sulphur.

It is possible to weld sheet nickel upon iron and steel; advantage is taken of this in the manufacture of "armor plate."

Nickel as coinage possesses three advantages which recommends it for the construction of coins of small value: (1) It requires enormous pressure to stamp out the coin. (2) Resists wear because of its being such a hard metal. (3) The commercial value of it is such that a much smaller-sized coin may be made from it than of copper and represent a greater value.

Arsenic, phosphorus, aluminum and magnesium considerably decrease the fusing point of nickel and do not interfere with its malleability except when present in excessive amounts.

Solubilities.—Hydrochloric and sulphuric acids, both dilute and concentrated, attack nickel but very slowly. Diluted nitric acid readily attacks it but concentrated nitric acid seems to render nickel passive. It is not attacked by alkali hydroxide or carbonates even when fused with them.

Compounds.—Nickel forms oxides corresponding to the formulas NiO , Ni_2O_3 , and Ni_3O_4 . The first is the only basic oxide. Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, is prepared by dissolving the oxide in sulphuric acid. This salt is used in electroplating of nickel.

Alloys.—Copper and nickel alloy, and this alloy is used as coinage for coins of small denomination; Belgium, Germany and United States coins consist of about 35 per cent. nickel and 65 per cent. copper.

Copper, nickel and zinc form German silver. German silver is used in the construction of orthodontic appliances and contains about 18 per cent. nickel; objection has been



raised to the use of this material because of it deteriorating in the fluid of the mouth. For further information upon this subject see *Items of Interest*, 1909.

German silver wire loses its elasticity upon heating and its rigidity can only be restored by working the metal.

Nickel is also used in some of the substitutes for platinum.

RESUMÉ.

Symbol, Ni.	Chief ore, garnierite.
Valency, II, III.	Conductivity of heat, 12.77.
Atomic weight, 58.68.	Coefficient of expansion,
Melting point, 1450° C.	0.000016.
Specific heat, 0.1092.	Ductility, 9th.
Malleability, 10th.	Conductivity, of electricity,
Color, white.	12.94.
Specific gravity, 8.8.	Tenacity, greater than iron.

CHAPTER XXII.

TANTALUM. TUNGSTEN.

THESE metals are classed as rare elements. Within the last few years tantalum has been introduced into dentistry for the construction of instruments as, for instance, spatulus for working silicate cements, and also instruments used in the application of drugs.

TANTALUM.

Occurrence.—Tantalum occurs widely distributed in nature. It is generally found combined as an acid oxide with other metals forming tantalates. The tantalates are usually associated with the columbites. The minerals, as a rule, are very complex in their composition, frequently containing manganese, iron, tin, calcium and several rare metals as tantalites or mixed tantalites and columbites.

Fergusonite, columbite, yttrotantalite and samorskite are some of these minerals.

Reduction.—The oxide Ta_2O_5 is extracted from the ores. This oxide is readily soluble in hydrofluoric acid. The oxide is converted into potassium tantalofluoride, K_2TaF_7 . When this salt is reduced a grayish-black metallic tantalum is obtained. The amorphous tantalum is then placed in an electric vacuum furnace and submitted to a very high temperature. From this process a very pure form of tantalum is obtained.

Properties.—The following properties were determined by Siemens and Halske: Melting point about $2770^{\circ} C.$; atomic

weight, 181.8; specific gravity, 16.6; coefficient of linear expansion, 0.0000079.

Tantalum is a very ductile and flexible metal and possesses a high tensile strength. It is about the same hardness as medium hard steel and is not magnetic; when heated in air its surface becomes covered with a yellow oxide and at 400° C. this changes to a blue color; at 600° C. it is grayish black and upon heating still higher it becomes completely oxidized.

Tantalum at a temperature sufficient to cause it to glow occludes hydrogen, nitrogen and other gases. When heated in chlorine it is converted into the chloride.

Tantalum pentoxide, Ta_2O_5 , is formed when the metal is heated in air or oxygen. When this compound is fused with fixed alkalies an alkali tantalate is formed. There is another oxide having the formula TaO_2 .

Tantalum chloride, $TaCl_5$, formed when the metal is heated in chlorine gas, is a volatile yellow solid. Melting at 211.3° and boiling at 241.6°. When the chloride is treated with water it decomposes, forming the hydrated acid, $2HTaO_3 \cdot H_2O$, ($H_4Ta_2O_7$).

Solubilities.—Nitric, hydrochloric, sulphuric acids or aqua regia are without action upon this metal. Hydrofluoric acid attacks the metal with the formation of the fluoride TaF_5 .

Solutions of the alkali hydroxides are without action, but when fused with the solid alkalies, alkali tantalates are formed.

Uses.—Tantalum instruments are very resistant to the action of corrosive agents. They may be sterilized by boiling with acid solutions, or may be heated to a low red heat. Iodine, phenol, sulphuric acid and cement liquids, which includes the most corrosive of agents used in dentistry, are without action upon this metal, consequently brooches and cement spatulas may be constructed of this metal. The following instruments have been placed upon the market made of tantalum: cement spatulas, brooches, burnishers, and in fact it is being tried out in almost all forms of instruments in which its properties recommend it.

TUNGSTEN.

Symbol, W. (wolfram).

Until within the last few years tungsten could not be produced in the degree of purity in which the metal possessed the properties of malleability and ductility. The electrical companies had obtained this metal in a brittle form and found that it could increase the lighting power of the older filaments used in incandescent globes and also at the same time conserve electrical energy. The statement has been made that a tungsten globe with the same candle power as the older (carbon) filament could be operated at a saving of 75 per cent. of electrical energy. The great drawback, however, was that the tungsten filament was exceedingly brittle and could not be subjected to jars or other disturbances which would tend to break the filament.

Within recent years malleable and ductile tungsten has been obtained. A study of its properties has led to the dental profession taking up this metal and attempting to adopt it to overcome some of the difficulties existing.

Dr. Price and F. A. Fahrenwald, in reports of the Research Department of the National Dental Association, have been conducting experiments upon this metal.

Occurrence.—Tungsten occurs in nature as the acid oxide combined with certain metals: Scheelite, CaWO_4 —in this mineral the tungsten is sometimes replaced by molybdenum; Wolframite, FeMnWO_4 . These minerals have been used in the past for making tungsten steel and also sodium tungstate which is used in rendering fabrics non-inflammable.

Reduction.—The ore is first concentrated and then receives a chemical treatment to produce tungstic acid.

Reduction from Wolframite.—The ore is first dressed and then treated with aqua regia or alkaline carbonates or alkaline acid sulphates. The following is the method used with sodium carbonate: The wolframite is heated in a reverberatory furnace with sodium carbonate; after fusing the mass is broken up and digested with boiling water. The

tungsten dissolves together with silicic and phosphoric acids as a silicotungstate and phosphotungstate of sodium. Hydrochloric acid is then added to the boiling solution and a series of chemical changes take place, resulting in the formation of tungstic acid. There are various other processes made use of in producing tungstic acid. Metallic tungsten may be obtained from tungstic acid by a variety of methods:

1. By reduction of tungstic acid by hydrogen.
2. By heating the trioxide with carbon in an electric furnace.
3. By heating to redness a mixture of ammonium tungstate or oxide with metallic zinc.

The tungsten as obtained by these processes is very brittle, containing impurities. The following is a condensed statement of the methods of preparing ductile and malleable tungsten as suggested by the various investigators of this subject: The product obtained by the above process is in the form of a black or gray powder. In order to render this tungsten in a coherent mass, the powdered metal is incorporated with a massing material, and then worked into a plastic form. This is then worked into a filament by forcing through a die and the filament is then heated to a high temperature so that nothing but pure tungsten remains.

The powdered tungsten may be pressed in a mold into bar form. The bar is then placed into a furnace and heated to 1300° C., hydrogen is passed through the furnace to prevent oxidation. It is then further heated in an electrical furnace under pressure in an atmosphere of hydrogen.

Properties.—Wrought tungsten is a bright, steel-colored metal, having a melting point between 3000° to 3200° C.; specific gravity, 19.3. Tungsten is hardened by working but not by heating and quenching. The metal may be annealed by heating to a white heat. It is non-magnetic, very tenacious and ductile. A wire may be drawn $\frac{1}{1000}$ of an inch in diameter. Its tenacity is several times that of steel and its hardness is such that the metal cannot be worked on a lathe or by hand. Tungsten is pliable, strong and tough, and moist or dry air is without action upon it.

Solubilities.—According to W. E. Ruder, wrought tungsten is insoluble in hydrochloric, sulphuric and concentrated nitric acids. Dilute nitric acid attacks it superficially with the formation of the yellow oxide. Aqua regia at ordinary temperatures oxidizes the surface of the metal and after boiling for four hours only 0.1 per cent. of tungsten was dissolved. The external surface becomes coated with the oxide which is not attacked by further additions of aqua regia.

Hydrofluoric acid does not attack this metal, but a mixture of hydrofluoric and nitric acids acts upon it.

Potassium hydroxide in the fused condition attacks the metal. The alkali carbonates when potassium nitrate is present and dissolves the metal somewhat.

Dental Uses.—Tungsten and molybdenum and tungsten alloys are at the present time being investigated as a possible substitute for platinum. Fahrenwald states: "Ductile tungsten and, to a lesser degree, ductile molybdenum meet all the specifications of a practical substitute for platinum and its alloys. These two defects are its ease of oxidation and the difficulty with which it can be soldered. And they may have been overcome by coating with a precious metal or alloy, the resulting material being in many ways far superior to platinum and its alloys." Tungsten has also been suggested for use as dowels in crown and bridge-work, as a much smaller gauge wire may be used, having the same strength as a large dowel constructed of some other metal. The wire is coated with gold so that it may be soldered. It has been suggested that the tungsten pin be coated with casting wax and introduced into the root canal. The dowel is then removed and gold is cast upon the dowel in the usual manner. Some of the tungsten dowels have had brittle spots which has caused the fracture of the dowel; however, there is no question but that these spots will be eliminated as the methods of producing wrought tungsten is improved upon.

Several solders for tungsten have been patented within the last few years. The description of the patents state that tungstates are made use of in the preparation of some of these.

CHAPTER XXIII.

ALKALI AND ALKALI EARTH METALS.

THE metals included in these groups, their atomic weight, symbol, and valencies are as follows:

ALKALI METALS.

	Symbol.	Valency.	Atomic weight.	Fusing point.	Specific gravity.
Sodium . . .	Na(Natrium)	I	23.0	95.6° C.	0.97
Potassium . . .	K(Kalium)	I	39.1	62.5	0.875
Lithium . . .	Li	I	6.94	180.0	0.59
Barium . . .	Ba	II	137.37	red heat	3.75
Strontium . . .	Sr	II	87.63	red heat	2.4
Calcium . . .	Ca	II	40.07	760(vacuo)	1.58
Magnesium . . .	Mg	II	24.32	750	1.74
Beryllium . . .	Be	II	9.1	1.85

SODIUM.

Occurrence.—This metal occurs widely distributed in nature in combination only. The principal minerals are the chloride; halite, NaCl ; sulphate mirabilite, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; nitrate, NaNO_3 ; carbonate; trona, $\text{Na}_2\text{CO}_3 \cdot \text{HNaCO}_3 \cdot 2\text{H}_2\text{O}$; fluoride cryolite, $3\text{NaF} \cdot \text{AlF}_3$.

Reduction.—Sodium may be obtained from its compounds: (1) By the reduction of the hydroxide with carbon. (2) By igniting the hydroxide with iron. (3) By gently heating carbonate with magnesium. (4) By electrolysis of the hydroxide.

Castner's Process.—The sodium hydroxide is run into an iron pot and kept in a molten state. The cathode passes through the bottom of the pot. The anodes are suspended from above. The products of electrolysis are hydrogen, oxygen and metallic sodium. The sodium is collected in

perforated ladles which allows the hydroxide to pass back into the pots, while the sodium because of its high surface tension remains in the ladle.

Properties.—Sodium is a soft metal which can readily be molded between the fingers. It decomposes in air, and because of this fact it is preserved under petroleum. When placed into water it combines with it, with the liberation of hydrogen.

Upon heating sodium volatilizes as a violet vapor. Sodium combines with mercury with violence, forming an amalgam. With liquid ammonia, sodium forms a blue solution.

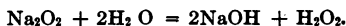
Compounds.—The compounds of sodium are of more importance than the metal, as they are used in metallurgical operations.

Oxides.—Sodium forms two oxides: sodium monoxide, Na_2O , and sodium peroxide, Na_2O_2 . Sodium monoxide is supposed to be formed when sodium burns in nitrous oxide at a temperature not above 180° . Sodium peroxide is a yellowish-white solid obtained by burning sodium briskly in oxygen. This compound is a very powerful oxidizing agent and when it comes in contact with organic material it frequently causes a rapid rise of temperature inducing rapid combustion and the production of a flame. Great care should be exercised in using this reagent.

Some reaction of sodium peroxide may be represented as following.



When an acid is present the following reaction occurs:



Sodium hydroxide, $\text{Na}(\text{OH})$, is prepared by treating sodium carbonate with calcium hydroxide. Sodium chloride, NaCl , is found in nature and may be prepared by treating sodium hydroxide with hydrochloric acid. When sodium chloride is strongly heated it fuses without decomposition. Sodium chloride is used to cover crucible charges in metallurgical operations, because in the fused condition it prevents the oxygen of the air from coming in contact with the crucible

contents. Sodium chloride is also used to convert certain metals into the chloride, for example, copper and silver.

Sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, is prepared commercially from the chloride by the LeBlanc or Solvay process. When this compound is fused with ores, carbon dioxide is given off and the oxide of sodium combines with the impurities in the ore, forming fusible compounds, thus acting as a flux. It is also used when in the fused condition to wash down the sides of the crucible and remove adhering particles. It combines with sulphur present in ores or is said to be a desulphurizing agent.

Sodium bicarbonate is prepared by the Solvay process. When heated it is converted into the carbonate and reacts similarly to that reagent. Sodium borate (sodium tetraborate), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. This is a natural occurring compound and is a very valuable flux. When heated borax fuses to a thin, limpid, liquid mass.

The salts of boric acid are very hard to volatilize, because of this fact they will replace, at a higher temperature, most of the other acids from combination. Sulphuric, nitric and hydrochloric acids are generally considered much stronger and harder to replace from combination with metals than boric acid. At an elevated temperature boric acid replaces all of these acids from combination. The oxides of the metals also combine with the boric acid and form fusible salts and as a result the salts of this acid are very useful as a flux. Sodium borate is frequently used in this capacity when operations are carried on at a temperature of red heat or greater. Disodium phosphate, $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$, is obtained by heating phosphoric acid with sodium carbonate. The phosphates also form a fusible compound and combine with metallic oxide similar to the borates. Microcosmic salt, $\text{NaNH}_4\text{HPO}_4$, on fusing forms NaPO_3 , sodium metaphosphate, and in the presence of metallic oxides combine to form double phosphates and pyrophosphates which are fusible.

Sodium nitrate, NaNO_3 , is found in nature; it may be prepared by treating sodium carbonate or hydroxide with nitric acid. Sodium nitrate is a white, deliquescent, crystalline

solid. It is a valuable oxidizing agent, and may be used to oxidize base metals from alloys of the noble metals. The oxide formed is then taken up by the flux thus removing contaminations from noble metals.

POTASSIUM.

Occurrence.—The metal occurs in nature only in combination. The principal compounds are: the chloride sylvite, KCl ; carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; nitrate, KNO_3 . It also occurs in many silicates and in the ashes of land plants.

Reduction.—The metal is obtained: (1) by heating a mixture of potassium carbonate and charcoal; (2) by electrolysis of the hydroxide or the cyanide.

Properties.—Potassium is a silver-white metal, very soft at ordinary temperature, but becomes brittle at 0° ; when heated, air being excluded, potassium boils and the vapor is emerald green. It reacts with water violently and the heat of the reaction is sufficient to cause the hydrogen given off to unite with oxygen of the air and a violet flame is produced. The metal oxidizes so readily that it must be preserved under naphtha. Potassium and sodium form a liquid alloy which is sometimes used in dentistry for the treatment of putrescent pulps and also to enlarge root canals. Potassium, like sodium, forms a great number of very useful salts. Potassium nitrate, KNO_3 , and the chlorate, KClO_3 , are used as powerful oxidizing agents, the latter salt must be handled with great care, as violent explosions have occurred in carelessly handling this compound.

Potassium Cyanide.—The cyanides are for the greater part all artificially prepared. They are particularly noted for their poisonous properties and for this reason should be handled with extreme care. Potassium cyanide is obtained from yellow prussiate of potash by heating in the presence of a reducing agent (chlorine or potassium carbonate). It is obtained in amorphous blocks of a grayish color. Potassium cyanide is readily soluble in water and the solution possesses the property of dissolving gold and silver when air is present.

Solutions of this salt are also used in electroplating. Potassium cyanide forms double salts with the cyanides of iron. Potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe_2(CN)_{12}$, are used in testing for iron, both quantitatively and qualitatively; the former salt is also used to some extent in tempering iron. Potassium salts are nearly all soluble, the exception to this rule is the compound formed with platinic chloride, potassium chlorplatinate, and the following: potassium fluosilicate, potassium perchlorate, potassium tartrate (slightly soluble).

LITHIUM.

Occurrence.—This metal occurs widely distributed but only in small quantities. Traces are found in quite a few minerals. It also occurs in small quantities in the vegetable kingdom.

Reduction.—Lithium is obtained from its compounds by the electrolysis of the fused chloride. The metal may also be obtained by igniting with metallic magnesium.

Properties.—Lithium is the lightest of known solids, having a specific gravity of 0.5936. It does not volatilize at red heat and is harder than sodium or potassium but softer than lead. Lithium may be drawn into wire or rolled into sheets. It does not react so violently as sodium and potassium and must be heated to 200° before it will combine with oxygen, it then burns, giving off a very intense white light. The salts of this metal impart a crimson color to the Bunsen flame.

Barium, Calcium, and Strontium.—These metals are of very little importance from a metallurgical point of view. They may be obtained by the electrolysis of their fused chloride. Their natural occurring compounds are often associated with the minerals of the more useful metals, and the removal of these compounds is often a problem which presents itself to the metallurgist. Calcium carbonate is often used to aid in the removal of silicates and other impurities in an ore of an acid nature.

Calcium sulphate is a natural occurring compound; this

mineral is known as gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Upon heating, gypsum loses some of its water of crystallization and a compound having the formula $(\text{CaSO}_4)_2\text{H}_2\text{O}$ is produced. This substance is known as plaster of Paris and possesses the property of again taking up moisture and setting to a hard mass through a process of crystallization.

Plaster of Paris is used, in conjunction with other materials, to form a refractory substance.

Calcium oxide, CaO , possesses great resistance to the action of heat. In the oxyhydrogen flame it glows and gives off an intense white light. Blocks made of this substance are used in melting platinum and other metals possessing high fusing points. Calcium carbonate, CaCO_3 , is used as a basic flux in the iron industry, it loses carbon dioxide and is converted into the oxide.

MAGNESIUM.

Occurrence.—Magnesium occurs as the sulphate, carbonate, and hydroxide. It is never found in the free state.

Reduction.—The metal may be obtained by the following process: (1) By the electrolysis of the chloride or sulphate. (2) By ignition of the chloride with metallic sodium or potassium.

Properties.—Magnesium is a white, hard, malleable and ductile metal, not acted upon by water or alkalis at ordinary temperature. When heated in air or oxygen it burns with incandescence to form the oxide MgO . When heated it combines directly with nitrogen, phosphorus, arsenic, sulphur, and chlorine. Metallic magnesium possesses the property of liberating the metals from combination and it may be used in the same capacity as aluminum (Goldschmidt process, thermite); however, metallic aluminum will liberate metallic magnesium from its compounds. It forms alloys with mercury and tin which decompose water.

Alloys of aluminum and magnesium are said to possess a very low specific gravity and also have an exceedingly high tensile strength.

Magnesium oxide, MgO , is a white infusible powder frequently used to line metallurgical furnaces. When this compound is mixed with a solution of magnesium chloride, MgCl_2 , the mass possesses the property of setting, forming a very dense substance.

BERYLLIUM.

Beryllium is a rare metal occurring as the silicate phenakite, Be_2SiO_4 , and in some other silicates. The metal is a white, malleable substance and is not acted upon by air at ordinary temperatures. It does not decompose water or steam even when heated to a red heat. Oxygen or sulphur scarcely attack it. The metal is soluble in acids except when in compact form, when nitric acid is without action upon it. Salts of this metal are claimed to be used in certain dental cements.

CHAPTER XXIV.

AMALGAMS.

AN amalgam may be defined as an alloy of two or more metals, one of them being mercury. The same law holds true for amalgams as for alloys in that they may be chemical compounds, mixed crystals, eutectics, or mixtures of all the above.

Mercury is a very peculiar metal, having the lowest fusing point of any metallic substance, and as this temperature is far below that of ordinary atmospheric conditions, it is rendered a liquid. When mercury is mixed with other metals it reduces their fusing point in a remarkable manner. Comparing the alloys of mercury with that of some other metals it will help to explain the phenomenon of amalgamation to a certain extent. Consider an alloy of lead, for example. When lead and higher fusing metals are alloyed, chemical compounds, etc., may be formed. It is possible to have the lead present in such excess that it will only carry minute quantities of some metal for which it has an affinity; now, if the lead solidified at the ordinary temperature of the atmosphere it would be possible to express the surplus quantity which is present and the resultant alloy remaining would then slowly congeal. On the other hand, if the surrounding temperature be kept to that at which lead fuses the same phenomenon will take place, that is, the surplus lead may be expressed.

When mercury is mixed with another metal it is possible to have the three conditions present (chemical compound formed, etc.), the surplus mercury may be expressed or, comparing with the lead analogy, the mass might be cooled to the fusing point of mercury and the entire mass would then solidify. With most amalgams we are working at the

temperature above the melting point of mercury and to remove this excess quantity pressure is used, thus leaving the metallic mass having the highest fusing point, then crystallization takes place and solidification results.

Setting of Dental Amalgams.—As in other alloys so with amalgams (the mercury when added to a mixture of metals or an alloy), there may be a greater adhesive force between the mercury and some particular metal and this force may be greater than the force of cohesion; in this case amalgamation readily takes place between the metals and mercury even at the exclusion of the other metals present.

Silver and mercury combine and form a chemical compound, and in the presence of a slight excess of mercury this compound combines with another portion of mercury, and when rubbed in the palm of the hand a gritting sound is given off, indicating that the mass is crystalline. The theory has been advanced that the same phenomenon takes place in the setting of an amalgam alloy, *i. e.*, that the crystals of amalgam first formed dissolve in a slight excess of mercury and then a new crystalline growth takes place causing the setting of the amalgam. Even after this takes place, there is no question but what future changes take place in an amalgam, and any factor which would tend to disturb the equilibrium existing after the primary setting will cause changes in the amalgam mass.

Behavior of Mercury toward Metals.—DIRECT COMBINATION.

—1. Mercury combines with some metals directly; in some cases there is every evidence of a chemical compound being formed. Sodium and potassium when heated to 440° combine with mercury with the formation of crystalline compounds having the formula Na_3Hg and K_2Hg . When combining there is frequently a violent reaction indicating chemical union. Mercury may combine readily with a metal without giving any perceptible evidence of a chemical change, but upon examination there may be found that compounds are formed. With tin the union is without any perceptible evidence of a chemical change, but, nevertheless, chemical compounds are formed.

2. Some metals only unite with mercury when they are in a finely divided condition. In fact most metals combine with mercury much more readily when in the finely divided state. To obtain the metal in this condition a soluble salt of the metal is used and a strip of a more electropositive metal is then placed in the solution; this causes the first metal to be thrown down in a finely divided condition. To illustrate, iron when placed in a solution of copper sulphate; zinc will have a similar effect upon silver solutions.

3. *Amalgamation by Indirect Means.*—Mercury will not unite directly with some metals, under these conditions amalgamation may be produced by treating the metal with a salt of mercury. In other cases a salt of the metal is treated with mercury. Mercury in the form of vapor combines with metals; if gold leaf be placed in the neck of a bottle containing mercury, even at ordinary temperatures, the vapor arising from the surface of the mercury will cause the whitening of the surface of the gold, showing that amalgamation has taken place even under these conditions.

Amalgams are sometimes named according to the number of metals they contain.

Binary amalgams contain one metal with mercury.

Ternary, quaternary, quinary having respectively two, three or four metals with mercury.

The simpler forms of amalgams are used for commercial purposes; tin amalgam in the construction of the cheaper forms of mirrors, gold is amalgamated and the mercury is then boiled off, giving the gold surface a characteristic appearance. Zinc amalgam is used to coat zinc poles of wet cells to prevent polarization. Through the formation of the amalgam silver and gold are separated from other metals and impurities in the recovery of these metals from their ores.

The more complex amalgams are used in dentistry as a filling material. An amalgam must possess certain requirements in order to be suitable for a filling material; among these the following may be enumerated:

1. After introducing into cavity it should possess permanency of form and absolute resistance to chemical substance.

2. Its color should not be objectionable.
3. It should possess good working qualities and be easily manipulated.

Permanency of Form.—Under permanency of form there are two phenomena to be considered:

1. Changes due to a lack of proper physical properties possessed by the amalgam.
2. Changes due to a lack of chemical resistance upon the part of the amalgam.

During the process of solidification an amalgam should not contract, for in so doing a faulty joint will be produced which will leave the tooth in such a condition that the factors which produce caries may again attack the tooth substance, causing recurrent decay, and the tooth will in no way be benefited by such a filling. Expansion to a very slight degree is permissible. However, expansion beyond this very limited degree will also cause faulty margins and leakage of the filling material will result. It should possess sufficient hardness to withstand the force of mastication and sufficient strength to retain its margins. Under stress amalgams possess the property of solid flow to a greater or less extent, this property should not be present in an appreciable amount, neither should the amalgam assume the spherical form; both of the factors tend to decrease the permanency of an amalgam filling.

Chemical agents in the mouth may attack an amalgam, forming salts which would cause a discoloration of tooth substance and also the fillings; in some cases these salts may be injurious to the general health of the patient. The amalgam should not possess too great a potential difference from that possessed by other filling materials used.

Color.—At the best, the color of amalgam can hardly be said to be unobjectionable; however, some amalgams are more unsightly than others.

Manipulation and Working Properties.—To the author this is one of the most important phases of this subject. Using an every-day expression, an amalgam should be "fool-proof."

There are a great many factors that influence the per-

manency of form of the amalgam filling; with the products as prepared by the better manufacturers of this article there is little room for doubt but that the poor showing of some amalgam fillings is, in great part, due to a lack of proper technic in incorporating mercury with the alloy. I have observed various operators manipulating amalgams and have found that, at best, this operation is carried out in a haphazard manner. If we were as careless in our manipulation of gold as we are with amalgams, gold certainly would have been considered years ago as a material totally unfit for filling purposes.

The working properties of an amalgam should be such that the proper contour may be given to the filling so that the lost parts of the tooth structure cannot only be reproduced but also correction of the deficiencies existing.

Discoloration.—The metals used in dental amalgams are attacked by hydrogen sulphide, which is present in the mouth to a greater or less extent. Both silver and mercury combine with this agent, forming black sulphides. If an alloy filling be placed so that it comes in contact with gold, the amalgam will be discolored; in this case the discoloration is due to electrolysis.

Tooth substance is also attacked by the metallic salts formed and upon examination it will be found that the contents of the dentinal tubule is colored black. This coloration may be due in part to the formation of sulphides and also to the effect of silver salts acting upon the albuminous materials present in the tubule. Leaky fillings will cause the retention of food material which undergo decomposition and the products formed attack the alloy with the production of metallic salts, these in turn will discolor the tooth. Noble metals when added to amalgam do not increase their resistance to such agencies.

Dental Amalgam Alloys.—A dental amalgam alloy is an alloy intended to be incorporated with mercury, to form an amalgam which is used as a filling material in dental operations.

These alloys may contain the following metals: silver, tin, copper and sometimes zinc, gold or platinum.

Certain terms are used in the study of amalgams. Their description follows:

Flow.—Amalgams are, as a rule, brittle bodies, and when pressure is applied in sufficient quantity fracture will result; however, under a more moderate pressure over a longer period of time amalgams may change their form. Dr. Black, in speaking of this phenomenon, states that amalgams are brittle, but are exceptions to the general rule in that they are also somewhat malleable. Flow then may be defined as the change in form of an amalgam under slow-continued pressure. Some amalgams seem to change their forms and attempt to assume a spherical shape. Liquids if unacted upon by external forces, tend to assume the spherical shape, as this geometrical form has the least surface for a given volume. In this case spheroiding is due to gravity.

Spheroiding.—Spheroiding is the term used to designate the property of an amalgam of attempting to assume the spherical form. Attempts have been made to explain the spheroiding of amalgams according to the same phenomenon as occurs in liquids.

Edge Strength.—Some amalgams are so brittle that they will not retain a fine edge and during the process of mastication this surface is fractured away and thus produces a faulty filling. Edge strength may be defined as that strength possessed by an amalgam to resist rupture at its margins. Some amalgams cannot be manipulated so as to retain a very fine margin. In this attenuated condition some are so brittle that they cannot withstand the force of mastication, in others the amalgam will form a rounded edge and this also is an objection. If proper regard has been taken as to cavity preparation, very little fear may be felt from this source in the better grades of alloys. In alloy fillings which have been *in situ* for some time it may be frequently observed that the margins are very irregular. This irregularity may be due to some of the causes already mentioned, *i. e.*: (1) Contraction of the alloy after inserting. (2) Slow changes

occurring after the first setting. (3) Lack of edge-strength. (4) Finally, the effect of the alloy upon the interprismatic substance of the enamel. The enamel at these margins is exceedingly brittle and it shows stain from the amalgam, and it is very evident that this factor has something to do with the faulty condition sometimes existing about the margins of old amalgam fillings.

As has already been stated, if the margins have received their proper bevel this trouble may be reduced to a minimum.

Aging.—Aging is simply a process of annealing a dental amalgam alloy. This process consists of uniformly heating the alloy to a certain temperature for a given length of time. It was at one time thought that by this operation the particles of the alloy were superficially oxidized; however, Dr. Black has proved that the heating simply causes an adjustment of the molecules of the alloy to their normal relations. As a result of the rapid cooling of the ingot and also the mechanical procedure used in reducing the alloy, a strained condition of the molecules exists. Just the same as in the case of annealing a piece of gold the normal arrangement of the molecules is brought about by heating, so in the case of these alloys. The aging of alloys, however, is a very particular process; the time and temperature are governed by the physical properties of the metals present in the alloy. The new mix of metals must be tested before the proper aging can be determined; from this we see that no set temperature or time may be stated.

If aging is carried too far it affects the working property of the amalgam, causing slow setting, and the alloy requires a smaller quantity of mercury to amalgamate and finally it may completely overcome the slight expansion and even cause the alloy to contract. Aging may be accomplished by heating to a higher temperature for a short time, but the results accomplished are not so uniform. Dental amalgam alloys age even at ordinary temperatures, and this may affect the properties of the alloy to such an extent as to completely change its physical properties and render same useless as a filling material. An alloy that is not aged by the manu-

facture would undergo a slow process of annealing upon standing and its properties would thus change from time to time and the product would not be one that could be depended upon. All that may be expected from this process is to overcome to a great extent those changes which would occur in the alloy as the result of heat and the time elapsing between the comminution and the inserting of the alloy as a filling material. Even alloys that have been aged should not be kept in stock for any length of time, as the aging which it receives may render its properties entirely different from those tested out by the manufacturer.

It is very good practice for the dentist not to purchase this material in too large quantities, but rather to replace his stock at shorter intervals of time.

Balanced Alloy.—A balanced alloy is one in which the physical properties of the alloy is so modified that when the amalgam prepared from it sets there will be no contraction, and in the strict sense of the term the amalgam should neither contract nor expand.

In the construction of a dental amalgam alloy silver is the expanding element and tin is the metal favoring contraction. When these two metals are alloyed in certain proportions, an attempt is made to have the expansion of silver neutralize the contraction of tin. *This is not balancing an alloy.* In order to produce a balanced alloy the metals are alloyed and the resultant alloy is tested as to its shrinkage or expanding properties; whichever condition exists, this amount of shrinkage or expansion is balanced by incorporating some other alloy possessing an opposite property. If the freshly prepared alloy contracts, then a sufficient quantity of an alloy which has been tested and found to expand is added, and in this way a balanced action as regards contraction and expansion is brought about. As aging favors contraction, and as a slight amount of expansion tends to insure a perfect joint between the amalgam and the cavity wall, most balanced alloys are prepared so as to expand slightly. The amount of this expansion is exceedingly small and is measured in $\frac{1}{4000}$ of an inch.

The alloying of metals for the preparation of dental amalgam alloy is not as simple as might be supposed. If these metals are fused in the ordinary way there is every liability of the metals oxidizing, and thus cause an alteration in the composition of the alloy. Special precautions must be taken in the selection of a suitable crucible, as contamination may be introduced from this source.

One method of producing this alloy consists of fusing the tin in an electric furnace in an inert atmosphere and then adding the silver and other constituents. This may be accomplished at a comparatively low temperature (dull red heat), while if the silver be first fused the temperature is so high that there is a probability of not obtaining a homogeneous mixture.

Great care is necessary to produce a homogeneous mixture. The writer has made it a practice for the last four or five years to have classes make a qualitative test of these alloys, and in two cases one-half of the class found copper and the other half absolutely could not obtain a test for this metal; homogeneity was lacking in these alloys.

After the metals have fused every precaution, by agitating, stirring and gradual cooling, should be used to insure a uniform mixture. The alloy is then poured into a suitable mold. The ingot is then reduced into filings or shavings, by suitable files or lathes. The process of reducing the alloy to a suitable form so as to be used is known as comminution. The alloy is then treated with a strong magnet to remove any steel which may have been introduced from the files. Care must be taken as to the condition of the filings or shavings, the more nearly uniform they are in size the more uniform will be the properties of the amalgam. This condition of the prepared alloy has a direct influence upon the quantity of mercury used and is indirectly a factor in expansion and contraction. The alloy is now ready for the aging process. The temperature at which the aging is produced is governed by the composition of the alloy and also the length of time to which it is subjected to the heating process.

Testing the Physical Properties of Dental Amalgam Alloys.

—A sufficient quantity of the alloy is placed in a porcelain mortar and about an equal weight of mercury is then added, the mass is then triturated until the mercury is thoroughly incorporated with the alloy, additional quantities of mercury are added until the amalgam possesses sufficient plasticity to be worked between the fingers without separating. When this degree of amalgamation has been reached the amalgam is removed from the mortar and thoroughly kneaded in the palm of the hand. The slight excess of mercury is then

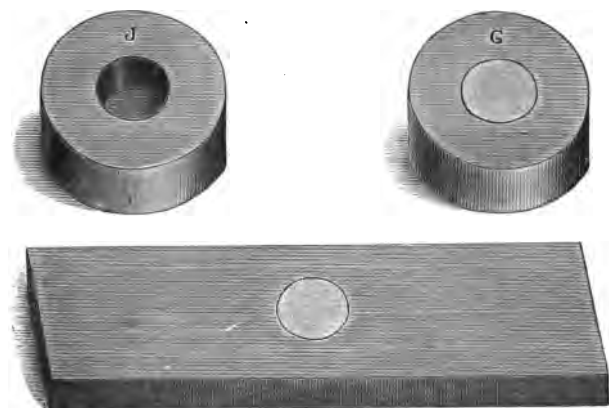


FIG. 59.—The Wedelstaedt steel test-tube, and one steel slide for the microscope.

removed by squeezing the amalgam in a chamois leather. The amalgam is then worked into a Wedelstaedt test-tube (Fig. 59). In this operation small pledgets of the amalgam are introduced at a time and mallet force is used to thoroughly condense the amalgam. The excess mercury separating from the amalgam from time to time is removed and then additional pledgets of amalgam are added and this operation is continued until the test-tube is completely filled. The margins are carefully finished and the amalgam allowed to set.

The Wedelstaedt test-tube is simply a steel block having a circular concavity of definite size and milled so as to have perfect margins. It is used as a receptacle for the amalgam while it is undergoing the hardening or setting process. Any changes produced about the margins may be observed by the use of the amalgam micrometer.



FIG. 60

Testing for Expansion and Contraction.—The amalgam micrometer (Fig. 60) is one gotten up at the suggestion of Dr. G. V. Black. The test-tube is placed under the lens and the conditions of the margins noted. The circular dial is connected with a pointer under the lens, and by the turning of the thumb-screw on the left of the platform the amount of change in the amalgam is recorded by the gradua-

tions on the dial. This is but one form of micrometer, and some of these instruments are so regulated that one point on the dial is equal to $\frac{1}{40000}$ of an inch. A point on this micrometer would mean a contraction or expansion of $\frac{1}{40000}$ of an inch. Some definite standard should be used as to the value of a point in all of the various makes of micrometers; the writer is very much in favor of adopting the value of a point as having the same value as a micron. In this way a comparison may be readily made with the size of the microorganisms, as this is the system of measurement made use of in bacteriology. Miller describes the *jodococcus vaginatus* as being 0.73 micron in thickness. *Spirillum sputigen* is described as 0.1 to 0.3 micron in breadth and 1 to 2.5 microns in length.

The diameter or width of the microorganisms have a direct bearing upon the standard to be arrived at as regards contraction or expansion of an amalgam. As microorganisms are the active factors in the cause of caries, the margins of a filling should be such as to exclude these agents to the highest degree. Considering the size of the *jodococcus* as 0.73 micron, which would be equivalent to about $\frac{1}{132600}$ of an inch, it becomes evident that an amalgam which contracts to the least degree would be absolutely worthless as a filling material. In the above case the mathematical calculation becomes comparatively easy when a point is equal to 1 micron. Taking a point as the value of 1 micron, then the above microorganism would of course have a breadth of 0.73 point. Dr. Crandall is using an instrument so graduated that a point is $\frac{1}{25000}$ inch. This more nearly approximates the value of a micron which has the value of $\frac{1}{25399.54}$ of an inch or in round numbers $\frac{1}{25400}$ of an inch. By using the point on Dr. Crandall's instrument as equivalent to the micron it would introduce an error of only 1.5 parts in a thousand; however, it would only be a simple matter to change the graduations on all of these micrometers to be exactly equal to the micron and then uniformity in measurement would be established.

Contraction.—As has already been stated, this property should be absolutely lacking in a dental amalgam. As the

amalgam alloys are now prepared this property is eliminated when the product leaves the factory, but the slow process of aging which the alloy receives upon standing, due to the agencies of heat, is liable to overcome the slight expansion originally possessed by the alloy and render the product a contracting amalgam.

Expansion.—A slight amount of expansion is beneficial; however, the exact amount can hardly be stated; some of the manufacturers claim that it should not exceed 0.6 micron. It is the author's opinion that this amount may be greatly exceeded even to the extent of 8 or 9 microns. The points to be considered in this case are:

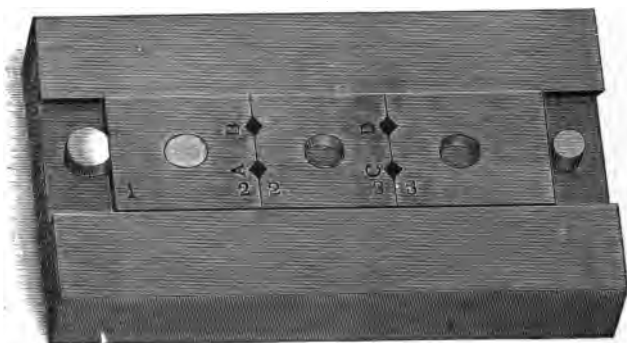


FIG. 61

1. If the amalgam does not expand sufficiently, it will not be permanent enough to withstand a sufficient amount of aging, while in the hands of the dental depots or the dentist, before using.

2. An excess of expansion would cause the filling to bulge from its margins.

Flow and Crushing Strength.—Suitable molds of definite size are used to obtain cubes of the alloy. Fig. 61 illustrates a set of these instruments as gotten up by Dr. G. V. Black. The cube is placed in the dynamometer (Fig. 62) and force applied by means of the thumb-screw *D*, the amount of

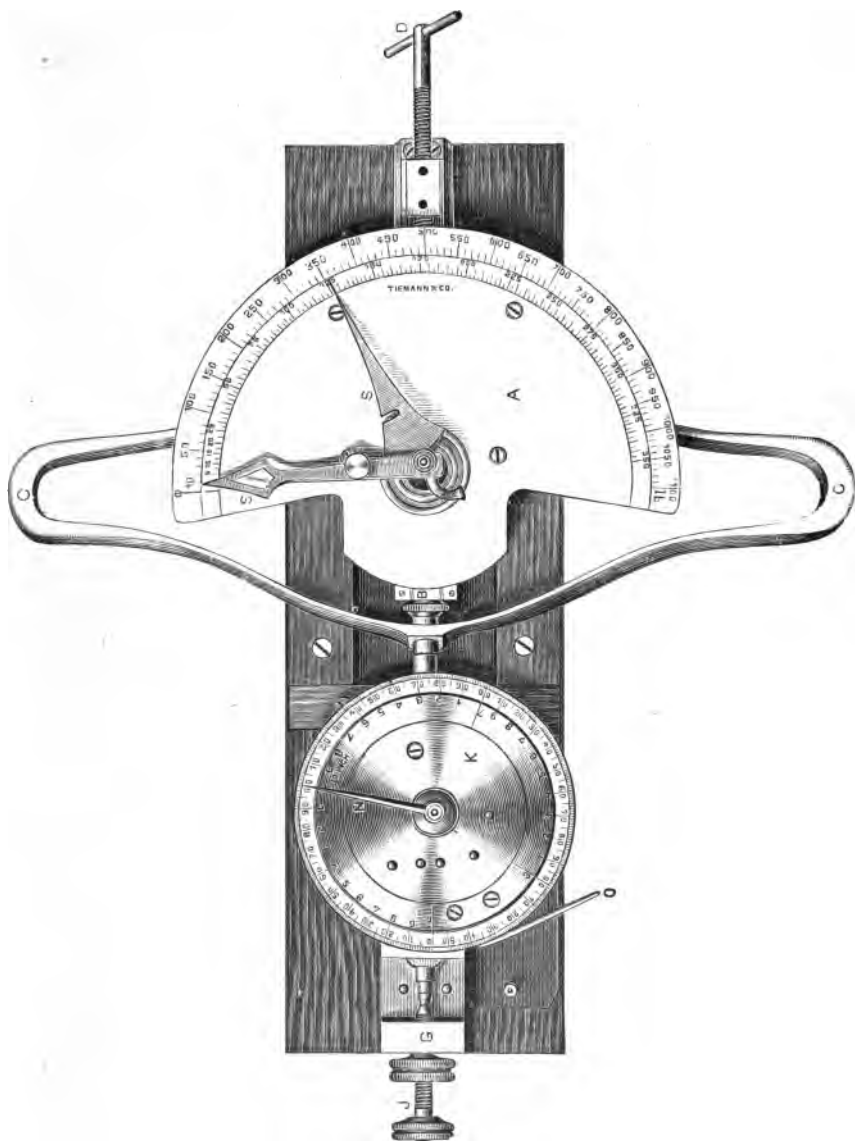


FIG. 62.—The dynamometer. The instrument in position for use.

force applied is recorded upon the dial *H*; the flow is recorded by adjusting the thumb-screw *J*, and upon reading the dial *K*, the amount of flow may be ascertained.

According to the experiments made at the Northwestern University, the average force of mastication as obtained from 1000 cases tested was 171 pounds. Taking this as a standard, amalgams should not show any appreciable amount of flow when this amount of pressure is applied. The result of an excessive flow in an amalgam would be such that the permanency of the filling would be impaired, and this property may be developed to such an extent as to fracture tooth substance. There must be a balance between flow and brittleness, as when flow is absolutely lacking brittleness is developed to such an extent that the amalgam will be low in crushing strength.

The amalgam should possess sufficient crushing strength in order to withstand the forces of mastication. This property is constantly subject to change at all times, and the strength of an amalgam filling will be found to have considerably decreased up to the time of six months after the insertion of the filling. This change should be expected to a greater or less degree, and to overcome this fault the freshly set amalgam should possess sufficient crushing strength, so that when this depreciation takes place the amalgam will still have sufficient strength to withstand the average 171 pounds of force exerted during mastication.

The method of manipulating the amalgamation has a direct effect upon this property. A mixture in which an excess of mercury has been used, and the excess not removed, will invariably result in a very brittle filling. An excessive amount of trituration tends also to weaken the amalgam; and still another condition which is of the greatest importance is the proper condensation of the amalgam.

Microscopic tests are also made use of in order to determine the crystalline structure and the degree of homogeneity of the amalgam. The observations may be made upon a fractured surface of a specimen of an alloy, or a second method may be used in which the surface of the amalgam is etched and highly polished and then placed under the microscope.

Mercury.—In the preparation of dental amalgam alloy every precaution is taken to have this product free from contaminations, and painstaking tests are made to render the physical properties of the amalgam as near perfect as our knowledge of the subject will permit. Just as much care is necessary in selecting the mercury as in the selection of the other metals. The use of ordinary commercial mercury is not a wise procedure, as it invariably contains metallic impurities which would tend to alter the physical properties of the amalgam.

The quantity of mercury used in amalgamation is also an important factor. If too little is used, a crumbly mass is produced which does not possess the sufficient amount of plasticity to allow the proper condensation necessary in introducing the filling. Such an amalgam is low in crushing strength.

When a large excess of mercury is used the composition of the alloy may be changed, due to the differences in solubility of the various metals making up the dental amalgam alloy. Upon squeezing out the excess of mercury tin will be lost to the greatest extent, while only a small quantity of silver will be carried by the mercury. The quantity of silver which may be lost in this way amounts to about 1.12 per cent. If the excess of mercury be not expressed at the time of introducing the amalgam, it will gradually be lost from the surface of the amalgam after setting and leave a brittle alloy having irregularities upon its surface.

A dental amalgam alloy requires the presence of a slight excess of mercury during the amalgamation process in order to insure a homogeneous amalgamation. The commercial products generally state the quantity of mercury which they have found by testing, as the correct amount, upon the circular enclosed with the alloy. It is best to use some form of measuring device in order to determine the quantity the operator is using; any other method of procedure is absolutely guesswork.

The object of amalgamation is not to dissolve all of the alloy in mercury but simply for the mercury to combine

with the surface of the alloy particles, and this amalgam upon setting acts as a cement to join the mass together. As the results of this there is actually only a comparatively small amount of amalgam setting, and this reduces the changes in volume which are produced during the crystallization to a minimum.

The mercury first combines with these surfaces and an additional quantity of mercury is gradually taken up; the latter product determines the setting property of the amalgam. If this additional quantity is taken up rapidly, it is generally indicative of a low silver alloy, as tin takes up mercury much more rapidly than silver. On the other hand, a slow amalgamating and setting alloy may indicate a high silver alloy. It must be borne in mind that the above is only approximately true, as other conditions may also cause this same effect; among these may be mentioned the degree of comminution and the aging of the alloy. Most of the manufacturers direct that a larger weight of mercury be used than alloy; however, after the slight excess of mercury has been removed by pressure, the alloy is present in a very slightly larger proportion than the mercury.

Properties of Amalgams.—*Tin.*—Tin combines very readily with mercury, forming quite a few chemical compounds. With large quantities of mercury a fluid amalgam may be obtained. The solid amalgams are said to expand upon setting. Tin amalgam does not possess sufficient crushing strength to be used as a dental amalgam. It also forms rounded margins and pulls away from the walls of a mold. However, when alloyed with silver it aids in amalgamation, and also tends to overcome the expansion of the silver during setting.

The following are the properties which tin is supposed to impart to dental amalgam: it assists in amalgamation, overcomes brittleness, increases flow, retards setting, lessens edge strength, aids in lightening the color and tends to cause contraction. When it is present in excessive amounts it renders the amalgam granular. The proportion of tin to silver, in which the expansion of the latter would overcome

the contraction of the tin, received a great amount of attention from Dr. Black. According to his determinations, alloys containing silver up to 64 per cent. contract; at 65 per cent. the contraction of tin is overcome, and this was considered the point at which a balance was obtained. Alloys containing more than 65 parts of silver expand. Fenchel shows by his experiments that alloys containing from 57.8 to 64.47 per cent. silver have the expansion of silver overcome by the contraction of tin. An alloy containing 72.5 silver expands the greatest of all of these alloys. As has already been stated in the balanced alloys, all that is expected of these metals upon alloying is to approximately balance the contraction and expansion, the deficiency is then overcome by other prepared alloys.

Silver.—Silver slowly amalgamates with mercury when in the massive form or as shavings; in the finely divided condition amalgamation takes place more rapidly. In the dental amalgam alloy silver ranks next to tin in its affinity for mercury.

According to Dr. Black,¹ a pure silver amalgam upon setting contracts for the first twenty-four hours; after this period of time has elapsed it remains stationary for from twelve to twenty-four hours and then slowly expands. This expansion which continues for three or four days finally is greater than the shrinkage in alloys containing but 40 per cent. of silver.

Silver is said to impart the following properties to a dental amalgam: it tends to form salts and causes discoloration of tooth substance and also darkens the amalgam; it tends to overcome contraction of tin; it increases the crushing strength, thus lessening flow.

Copper.—Copper amalgamates slowly, and in order to form an amalgam indirect methods of amalgamation are used. The copper is thrown down from the solution of the sulphate by metallic iron, and amalgamation is started by adding mercuric nitrate solution. After the amalga-

¹ Dental Cosmos, vol. xxxviii, p. 82.

tion is started, metallic mercury added and heat applied, copper amalgam is obtained. This amalgam was at one time extensively used as a filling material. The method of working differed from that used in the manipulation of our present-day amalgams. Copper amalgam was put upon the market in lozenge shape and when used was heated in an iron spoon; the excess of mercury was then expressed after the mass had been triturated. It behaved in a very peculiar manner; some fillings would preserve their margins beautifully, and the tooth substance would show very little, if any discoloration; it would not change form under the stress of mastication and seemed to possess germicidal properties in preserving the tooth from future decay; the external surface of the filling quickly became coated with the sulphide and turned black; however, this coloration did not penetrate the tooth. In other cases it produced poor margins, stained the tooth, causing a dark discoloration, showing every evidence of a leaky filling and under these conditions it appeared absolutely unsuited for filling purposes. The copper amalgam required great care in producing good margins, but it was the common belief that good margins once formed with the material remained in this condition and were not subject to changes. Because of this difference in behavior of copper amalgam some operators were strong in their praise, while those who met with the second set of phenomena were equally severe in their condemnation of this material.

In all possibility this difference in the behavior of copper amalgam was due for the most part to the improper preparation of the amalgam and, secondly, to the lack of proper care on the part of the operator in inserting the filling.

Copper amalgam is used at the present time for the construction of small dies or models in swaging diaphragms for crowns, construction of models in the indirect method of cast inlay work and various other forms of dies in which light swaging is used.

Copper is added to dental amalgam alloy to increase hardness and edge strength; it also aids in the setting qualities.

It, however, has a tendency to cause the amalgam to discolor. In the percentage in which it is used in most amalgams this objection is more than overbalanced by the beneficial properties which it imparts. These three metals are agreed upon by all as being necessary constituents of dental amalgam alloys; however, other metals are added for the purpose of modifying color, aiding in the working properties and for various other reasons.

The quantity of these additional metals rarely amounts to 5 per cent. or over of the weight of the dental amalgam alloy.

One of the great objections to adding too many metals in the production of the alloy is: as the number of metals present in an alloy increases, the difficulty of obtaining a homogeneous mass increases, and it must be borne in mind that each additional metal added just renders a homogeneous alloy that much harder to be obtained. The problem confronting us is simply this: "Does the addition of a certain metal with the properties which it imparts overbalance the difficulty of obtaining a homogeneous alloy?"

Zinc.—This metal at the present time is looked upon with disfavor by some, claiming that it causes great but slow contraction. Others have not lost their faith in this metal, claiming it toughens the amalgam and also tends to lighten the color.

Gold.—This metal has been discarded by most manufacturers. However, there are some that still are of the belief that the properties which it imparts to the alloy cannot be dispensed with. Among the desirable properties which are claimed for this metal are: toughness, increased working properties, and that it produces good edge strength.

Platinum.—Platinum is said to improve an amalgam when gold is present. When gold is not present it does not possess any beneficial properties; on the other hand, it is deleterious, causing a slow setting and tendency to shrink. In amalgamating such an alloy the hands are discolored or blackened by the presence of this metal.

Palladium, bismuth, antimony, cadmium, produce more harmful than beneficial properties in these alloys.

Cadmium forms an adhesive amalgam. However, it decomposes in the oral secretions with the formation of yellow cadmium sulphide, causing a yellow discoloration of tooth substance.

The composition of dental amalgam alloy may approximately be stated as follows: Silver 65, tin 30 and the various other metals making up the remaining five parts. If zinc is used it should not exceed 1 to 1.5 parts, while copper is permissible in a larger proportion.

In the author's opinion gold and platinum may be dispensed with, as the complexity of the alloy is so much increased by the addition of these two metals that the properties reputed to them do not justify their addition. However, the usefulness of the metals gold, platinum, and even zinc is simply a matter of opinion, and there is no question but what alloys possessing these metals, if properly manipulated by the dentist, will produce all that may be desired.

CHAPTER XXV.

METHODS OF DRY ANALYSIS.

A COURSE of dry analysis, or so-called blow-pipe analysis, is of importance to the dental student for several reasons: (1) It imparts a thorough working knowledge of the Bunsen flame. (2) It teaches the use of the mouth blow-pipe and cultivates the art of proper breathing in the use of same. (3) It impresses upon his mind the various phases of oxidation and reduction that are possible during the process of heating. (4) It instills a knowledge of chemical reactions which differ materially from those produced by wet methods.

Fusion.—The hottest portion of a flame is just beyond the tip of the blue flame. The reactive fusing point of the substance should be treated in one of the following ways:

- (a) If metallic, heat on the charcoal block.
- (b) If stony or vitreous, hold in the Bunsen flame by means of platinum-pointed pliers.
- (c) If a powder, make a paste with water and allow to dry on charcoal block and then heat.

Flame Coloration.—Use a platinum wire and hold in the flame of the Bunsen burner until all color disappears, then moisten the wire with some of the material; in some cases the color of the flame may be intensified by moistening a solid substance with a few drops of concentrated hydrochloric acid. The colors will be given under each metal in the list which follows.

Volatilization.—Some of the metals or their compounds are oxidized upon heating. The color of the sublimate or the odor produced is used to identify these substances. Volatilization tests are commonly obtained on charcoal, plaster, or in open and closed glass tubes. The reactions produced may be varied by the use of fluxes. Sodium carbonate or bismuth flux¹ may be used in these reactions.

¹ Two parts sulphur, one part potassium iodide, one part acid potassium sulphate.

Bead Tests.—In these tests a loop is made in a platinum wire mounted in a glass rod. The agent used to form the bead is borax, or microcosmic salt ($\text{NaNH}_4\text{HPO}_4$). The color of the bead produced varies, dependent upon the nature of the flame in which it is heated.

Bulb Tube Tests.—These tests are performed in two ways: 1. By simply heating the substance in a bulb tube and noticing the changes produced, such as the gases given off, formation of a sublimate, or charring.

2. Sulphuric acid may be added and the effects produced noted.

The following is a list of the more common metals and their characteristic reactions as produced in this form of analysis:

Antimony:

ON CHARCOAL, REDUCING FLAME—VOLATILE WHITE COAT,
BLUISH IN THIN LAYERS.

With Bismuth Flux:

On plaster: Peach-red coat.

On charcoal: Faint yellow or red coat.

In open tube: Dense, white, non-volatile, amorphous sublimate.

Flame: Pale yellowish green.

Arsenic:

On smoked plaster: White coat crystalline.

On charcoal block: Very volatile, white coat and strong garlic odor.

With Bismuth Flux:

On plaster: Reddish-orange coat.

On coal: Faint yellow coat.

Bismuth:

On charcoal: In either flame, a brittle metal and volatile; coat, dark orange-yellow, hot lemon-yellow, cold with yellowish-white border.

With Bismuth Flux:

On plaster: Bright scarlet coat, surrounded by chocolate brown. The brown may be made by ammonia.

Aluminum:

With sodium carbonate: Swells and forms an infusible compound.

With borax: Bead clear or cloudy, never opaque.

With cobalt solution and heated with blow-pipe: Fine blue color when cold.

Cadmium:

On charcoal, reducing flame: Dark brown coat, greenish yellow in thin layers.

On smoked plaster with bismuth flux: White coat made orange with ammonium sulphide.

Copper:

On coal with reducing flame: Formation of red malleable metal.

Flame: Emerald green or azure blue.

If the compound be moistened with hydrochloric acid the Azure-blue flame is produced.

With borax bead: Oxidizing flame. Green, hot, blue or greenish blue, cold.

Reducing flame: Greenish or colorless hot, opaque, and brownish red, cold.

Iron:

On charcoal, reducing flame: Many compounds become magnetic, sodium carbonate assists the reaction.

With borax beads: Oxidizing flame. Yellow to red, hot, colorless to yellow, cold.

Reducing flame: Bottle green.

Lead:

On charcoal: In either flame is reduced to malleable metal and may have lemon-yellow coating surrounding the lead button.

With Bismuth Flux:

On plaster: Chrome-yellow coat, blackening with ammonium sulphide.

On charcoal: Volatile yellow coat.

Flame: Azure blue.

Lithium:

Flame: Crimson, best obtained by heating near center of the flame.

Magnesium:

On charcoal with sodium carbonate: Insoluble, and not absorbed by the coal.

With Cobalt solution: Strongly heated becomes a pale flesh color.

Manganese:

With Borax Beads:

Oxidizing flame: Amethyst color, hot, reddens on cooling.

Reducing flame: Colorless or with black spots.

With sodium carbonate and potassium nitrate bead:

Oxidizing flame: Bluish green and opaque when cold.

Mercury:

With Bismuth Flux:

On plaster: Volatile yellow and scarlet coat if strongly heated; coat is black and yellow.

On charcoal: Faint yellow coat at a distance from the depression in the charcoal.

Nickel:

On charcoal reducing flame: The oxide becomes magnetic.

With borax bead:

Oxidizing flame: Violet, hot, pale reddish, cold.

Reducing flame: Cloudy and finally clear and colorless.

Potassium:

Flame: Violet.

Silver:

On Charcoal: Reduction to a malleable white metal.

Dissolve button in HNO_3 , dilute and add ammonium hydroxide slowly until the brown precipitate which first forms just dissolves, add 2 drops of solution of formaldehyde and heat in test-tube; mirror of silver will be produced.

Sodium:

Flame: Strong yellow flame, not visible through cobalt glass.

Strontium:

Flame: Intense crimson, improved by moistening with HCl.

Tin:

On charcoal:

Oxidizing flame: The oxide becomes yellow and luminous; when the oxide is moistened with cobaltous nitrate and heated with reducing flame the coat will be bluish green when cold.

Zinc:

On charcoal:

Oxidizing flame: The oxide becomes yellow and luminous while hot and upon cooling is colorless. When oxide is moistened with cobalt-nitrate solution and heated in reducing flame, the coat is yellowish green when cold.

The following is a systematic scheme for qualitative blow-pipe analysis:

TEST I.—Heat a portion of the substance gently with the oxidizing flame upon a charcoal block or a plaster tablet which has been blackened in the lamp flame. Arsenic and antimony will be recognized by the white coating.

TEST II.—Mix some of the substance with metallic sodium by means of a knife blade, ignite carefully on charcoal and heat residue with blow-pipe flame to obtain coating or to fuse together any metallic particles. Or mix a portion with soda and a little borax and heat strongly upon charcoal with reducing flame for three or four minutes. Arsenic, antimony, cadmium, zinc, and tin will be recognized by their characteristic reactions.

Residue Left on Charcoal.

Crush and examine for (1) magnetic particles; (2) metallic buttons; (3) place some of residue on silver coin.

1. Will show iron, nickel or cobalt.
2. Will show silver, lead, tin, copper, gold, bismuth or antimony.
3. Will show sulphur, selenium, tellurium.

TEST III.—Mix substance with a larger quantity of bismuth flux and heat on plaster tablet with oxidizing flame. Lead, mercury, bismuth, and antimony will show characteristic colorations.

TEST IV.—Dissolve the substance in microcosmic salt bead in the oxidizing flame, then heat three or four times in the reducing flame; note colors hot and cold, then reoxidize and note colors hot and cold.

Iron, Titanium, Molybdenum and Tungsten: The bead in oxidizing flame, cold is colorless or faint yellow.

Uranium, Vanadium and Nickel: The bead in oxidizing flame, cold is yellow or greenish yellow.

Manganese: The bead in oxidizing flame, cold is colored violet.

Chromium: In oxidizing flame is colored green.

Copper and Cobalt: In oxidizing flame is colored blue.

Barium, Calcium, Strontium, Magnesium: In oxidizing flame give white opaque beads.

TEST V.—Cupellation for silver and gold. Fuse one volume of the roasted substance on charcoal with one volume of borax glass and one or two volumes of test lead in reducing flame for about two minutes. Remove button and scorify it in reducing flame with fresh borax; then place button on cupel and blow oxidizing flame across it, using as strong blast and as little flame as are consistent with keeping the button melted. If the oxide of lead formed is dark or if the button freezes before brightening, scorify it again with borax and add more test lead, again cupel until there remains only a bright spherical button, unaltered by further blowing. If silver is present, the button is white, while if gold is present, the button is yellow or white.

TEST VI.—Heat substance with acid potassic sulphate. Oxides of nitrogen, bromine, chlorine and iodine will be recognized by their odor.

TEST VII.—Heat the substance gently with water to remove air and then add dilute hydrochloric acid. Carbon dioxide, hydrogen sulphide and hydrogen may be given off

TEST VIII.—Make a paste of the powdered substance with strong hydrochloric acid. Treat on platinum wire in the non-luminous flame of the Bunsen burner.

The colors produced are:

Metal.	Color.	Color through cobalt glass.
Sodium	Yellow	Invisible.
Potassium	Violet	Reddish violet.
Sodium and potassium	Yellow	Reddish violet.
Barium	Yellowish green	Bluish green.
Molybdenum		
Boron		
Calcium	Red	Greenish gray.
Strontium	Scarlet	Violet.
Copper	Azure blue	Azure blue.
	Emerald green	Emerald green.

TEST IX.—Heat the substance in a closed tube:

Water: Moisture in the side of tube.

Mercury: Metallic mirror collecting in globules.

Arsenic: Metallic mirror, no globules.

TEST X.—Treat finely powdered substance in test-tube with strong hydrochloric acid.

Effervescence: Carbon dioxide, hydrogen sulphide, sulphur dioxide, or hydrochloric acid may be given off; a gelatinous residue indicates a silicate.

CHAPTER XXVI.

WET METHOD OF ANALYSIS.

IN analyzing an alloy, the first procedure is to obtain a solution of the alloy with some suitable solvent. Hydrochloric or sulphuric acids, both dilute or concentrated, may be tried and if they fail to dissolve the alloy, then nitric acid may be tried. When nitric acid is used the solution should be evaporated to dryness in order to drive off the excess of the acid, as it would interfere with the action of hydrogen sulphide.

Alloys containing antimony and tin will produce a white precipitate when nitric acid is used, due to the formation of oxides of these metals. In such an alloy hydrochloric acid should be used first to dissolve these metals, and if the alloy is not entirely soluble then the metallic residue may be treated with nitric acid and dissolved. The outline for the separation of the metals is based upon the following reaction of them to certain reagents:

Hydrochloric acid precipitates silver, lead (partially) and mercurous mercury as the chlorides. Hydrogen sulphide in an acid solution throws down the following metals: bismuth, copper, cadmium, mercuric mercury, arsenic, antimony, tin, gold and platinum.

Hydrogen sulphide in an alkaline solution precipitates iron, aluminum, chromium, cobalt, nickel, manganese and zinc.

Ammonium carbonate precipitates barium, strontium, and calcium. The remaining metals, sodium, potassium, lithium and magnesium require special treatment in order to identify.

A confirmatory test is one that is used to positively identify a metal by the use of some special reagent. They are some-

times spoken of as "a test for the metal." To illustrate: potassium ferrocyanide in an acetic acid solution is a confirmatory test for copper. If it is desirable to make a simple test for one metal as in the case of a salt, or one wishes to determine if some particular metal is present, all that is necessary is to turn to the general analysis and use the reagents of some particular metal.

GROUP I.

Three metals are included under this heading, namely: lead, mercury in the mercurous condition designated as Hg_2 ; silver, Ag; they are alike in their behavior toward hydrochloric acid, HCl . This reagent added to a solution of one or more of these metals causes a white precipitate. Pb appears as white plumbic chloride, PbCl_2 , slightly soluble in cold but more soluble in hot water. Hg_2 as white mercurous chloride (calomel), Hg_2Cl_2 , insoluble in hot or cold water, and Ag as white argentic chloride, AgCl , insoluble in hot or cold water. They may be identified by characteristic precipitates. Pb forms white insoluble plumbic sulphate, PbSO_4 , Hg_2 , black, insoluble mercurous amido chloride, $\text{Hg}_2\text{H}_2\text{NCl}$, and white, insoluble AgCl .

Analytical Procedure.—Put 50 c.c. of cold solution of these metals into a 100 c.c. beaker and cautiously add concentrated HCl until a drop fails to cause a precipitate. Let stand five minutes. Filter into a 250 c.c. flask and keep the filtrate for the next group. The precipitate consists of the chlorides of group I metals; wash it once with cold water and reject the wash water. Next wash with 25 c.c. of hot water, passing it through the paper two or three times, PbCl_2 dissolves; cool the solution in a test-tube and add a few drops of dilute H_2SO_4 . If Pb is present, white insoluble PbSO_4 will appear.

Pour over the remaining precipitate, which is insoluble in hot water, 15 c.c. of ammoniac hydroxide, $(\text{H}_4\text{N})\text{OH}$, passing it through the paper two or three times. Hg_2Cl_2 , if present, is converted into a black $\text{Hg}_2\text{H}_2\text{NCl}$.

Note.—Hydrogen sulphide, H_2S , when present in the atmosphere of the laboratory, often causes a slight darkening even when Hg_2Cl_2 is absent. A distinction; therefore, must be made between the pronounced black of Hg_2H_2NCl and any slight change of color by H_2S . At the same time that $(H_4N)OH$ produces this black compound it dissolves $AgCl$.

Note.—If any $PbCl_2$ remains because of incomplete washing with hot water $(H_4N)OH$ will change to insoluble white basic plumbic chloride, $PbCl_2 \cdot Pb(OH)_2$, which renders the filtrate milky; as this does not interfere with the final test for Ag it may be disregarded.

Add conc. HNO_3 to the filtrate until all $(H_4N)OH$ is neutralized and the solution is acid; Ag , if present in quantity, appears as white, curdy $AgCl$; traces cause an opalescence.

GROUP II.

Ten metals, divided into subgroups A and B, are included under this heading, viz.:

- | | | |
|-------------|---|---|
| Subgroup A. | { | 1. Mercury in the mercuric condition designated as Hg . |
| | | 2. Lead, Pb . |
| | | 3. Bismuth, Bi . |
| | | 4. Copper, Cu . |
| | | 5. Cadmium, Cd . |
| | | 6. Arsenic, As . |
| | | 7. Antimony, Sb . |
| Subgroup B. | { | 8. Tin (<i>a</i>) Stannous $SnII$; (<i>b</i>) Stannic $SnIV$. |
| | | 9. Gold, Au . |
| | | 10. Platinum, Pt . |

They are alike in their behavior toward hydrogen sulphide, H_2S , as they are precipitated by this reagent from an acid solution. Under these conditions sulphides are formed, namely:

- | | | |
|-------------|---|---|
| Subgroup A. | { | 1. Hg appears as black mercuric sulphide, HgS . |
| | | 2. Pb appears as black plumbic sulphide, PbS . |
| | | 3. Bi appears as brown-black bismuthous sulphide, Bi_2S_3 . |
| | | 4. Cu appears as black cupric sulphide, CuS . |
| | | 5. Cd appears as yellow cadmic sulphide, CdS . |
| | | 6. As appears as yellow arsenous sulphide, As_2S_3 . |
| | | 7. Sb appears as orange-red antimonous sulphide, Sb_2S_3 . |
| Subgroup B. | { | 8. $SnII$ appears as chocolate-brown stannous sulphide, SnS . |
| | | 9. $SnIV$ appears as yellow stannic sulphide, SnS_2 . |
| | | 10. Au appears as brown sulphide, Au_2S or Au_2S_3 . |
| | | 11. Pt appears as black sulphide, PtS or PtS_2 . |

They may be identified by characteristic tests, viz.:

Subgroup A: (1) Hg, by (a) Hg globules: (b) white ppt. Hg_2Cl_2 . (2) Pb, by white ppt. PbSO_4 . (3) Bi, by white ppt. $\text{O} = \text{Bi} - \text{Cl}$. (4) Cu, by (a) blue $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; (b) red-brown ppt. $\text{Cu}_2\text{Fe}(\text{CN})_6$. (5) Cd, by yellow ppt. CdS .

Subgroup B: (6) As, by shiny brown-black mirror. (7) Sb, by orange-red ppt. Sb_2S_3 . (8) SnII and SnIV, by white ppt. with Hg_2Cl_2 . (9) Au, by precipitate with stannous and stannic chlorides (purple of Cassius). (10) Pt, by yellow ppt. with $(\text{H}_4\text{N})\text{Cl}$ ammoniac chloroplatinate.

Analytical Procedure.—The filtrate in a 250 c.c. flask from the HCl ppt. should be gently warmed upon the iron plate; or a solution free from the bases of group I should be acidified with HCl and treated in the same way. Next pass H_2S through the solution until it smells strongly of the gas after being thoroughly shaken. The metals of group II are precipitated as sulphides.

Note.—Complete ppt. is important, the solution must not be too strongly acid. An excess of H_2S must be used. Filter, add a few cubic centimeters water, warm gently and again treat with H_2S . If there is no ppt. the next step may be taken, otherwise dilute the remaining solution and pass more H_2S through it; this must be repeated until ppt. is complete. Filter into a 250 c.c. flask and keep the filtrate for group III. The color of the ppt. may indicate the presence or absence of certain metals. If it is black no information is given beyond the fact that at least one of the black sulphides is present. If it is yellow, black sulphides are absent except, possibly, in traces, and the color is due to Cd, As, Sb, or SnIV. Wash the ppt. three times with boiling water and transfer it to a small dish.

Note.—The method of procedure from this point depends upon whether metals of both subgroups or of one are present.

Procedure when Both Groups are Present.—Pour over the ppt. 15 to 25 c.c. of yellow ammoniac disulphide, $(\text{H}_4\text{N})_2\text{S}_2$, warm on the steam bath for five minutes and then stir frequently. This reagent dissolves subgroup B sulphides

but not those of subgroup A. Filter into a small beaker and keep the filtrate for subgroup B tests. Wash the ppt. with hot water three times. Transfer it to a small dish and make subgroup A tests.

Procedure when Subgroup A Alone is Present.—When subgroup B has been removed pour over the ppt. 15 to 25 c.c. of dilute HNO_3 and then add the same volume of water. Warm on the steam bath for ten minutes and stir frequently; all of the sulphide of subgroup A except HgS are dissolved. Filter into a beaker. Add to the filtrate 5 c.c. of diluted H_2SO_4 , pour it into a small dish and evaporate on the iron gauze until all HNO_3 has been expelled and the solution has nearly reached dryness. During this evaporation examine the ppt. for Hg. Wash it once with hot water. If the ppt. is not black but yellow, Hg is absent and the ppt. is sulphur. On the other hand, a black ppt. is not sufficient proof of Hg, since sulphur mixed with some undissolved sulphides other than HgS may be taken for HgS . Two tests are available for confirming the presence of Hg.

Copper Wire Test for Hg.—Put a few crystals of potassic chlorate, KClO_3 , into a test-tube and add 5 c.c. of conc. HCl , warm and pour over the HgS . Collect the acid solution in another test-tube and pass it through the paper two or three times until nothing but sulphur remains. Dilute the acid solution with the same volume of water and divide it into two portions, keep one portion for the next test for Hg. Place in the other a bright piece of copper wire, remove the wire after five minutes and dry it on the filter paper. Place it in a bulb tube and heat it; with a lens examine the cool part of the tube for globules of Hg which prove the presence of this metal in the mercuric condition.

Stannous Test for Hg.—To the reserved portion of the dilute acid solution add a few drops of a solution of stannous chloride, SnCl_2 ; a white ppt. of Hg_2Cl_2 often darkened by Hg proves the presence of Hg in the mercuric condition.

Return to the solution which has been evaporating, transfer it to a small beaker and wash any ppt. from the dish with cold water. A white ppt. is PbSO_4 and it is due to Pb

not completely removed by HCl in group I. *Note:* If Pb is found in group I it must appear here also, otherwise there has been some error in procedure. Pb when present in small amount may fail to appear in group I and yet appear in group II. If present and not removed it may cause trouble later in the analysis. Filter to remove PbSO_4 and collect the filtrate in a small beaker. Add $(\text{H}_4\text{N})\text{OH}$ until the solution is alkaline. This reagent may produce two results, namely:

(a) It may turn the solution blue, which is positive proof of the presence of Cu. (b) It may cause a flocculent ppt., which is an indication of Bi. *Note:* Cu may be present in such small amount that $(\text{H}_4\text{N})\text{OH}$ will not give the test. In this case the $\text{K}_4\text{Fe}(\text{CN})_6$ test must be made. If $(\text{H}_4\text{N})\text{OH}$ does not cause a ppt., Bi is absent. On the other hand a ppt. must not be accepted as proof of Bi until the confirmatory test has been made. Filter and collect the filtrate in a test-tube. If the filtrate is not blue take one-third of it and acidify with acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$). Add a few drops of a solution of $\text{K}_4\text{Fe}(\text{CN})_6$; a red-brown ppt. or coloration is due to cupric ferrocyanide, $\text{Cu}_2\text{Fe}(\text{CN})_6$, and proves the presence of Cu; keep the remaining two-thirds of the filtrate for the Cd test.

Wash the ppt. which may be bismuthous hydroxide, $\text{Bi}(\text{OH})_3$, twice with hot water. Set the funnel in a test-tube and pour over the ppt. five drops of conc. HCl. Pass it through the paper two or three times until the ppt. is dissolved. Add one drop of this solution to a test-tube full of water. A white ppt. is bismuthous oxychloride, BiOCl , and proves the presence of Bi.

Return to the remaining two-thirds of the filtrate and test it for Cd. If Cu has not been found by either test, pass the H_2S through the filtrate and a yellow ppt. of CdS appears if Cd is present. On the other hand, if Cu has been found by either test, add to the solution a few pieces of solid potassic cyanide, KCN.

If the solution is blue, enough KCN should be used to discharge the color. Pass H_2S through the solution. Yellow

CdS appears if Cd is present, but CuS is not ppt. in the presence of KCN.

Note.—In testing for Cd it often happens the ppt. is black instead of yellow. This arises from some error of manipulation resulting in the incomplete removal of one or more of the metals having black sulphides. Collect the ppt. on a filter paper of the smallest size and wash it twice with boiling water. Place the ppt. and paper in a dish and add 5 c.c. of diluted HNO_3 ; further dilute with the same volume of water. Warm on the water-bath, filter and evaporate with diluted H_2SO_4 , proceed as previously directed for removal of Pb and Bi. Finally pass H_2S through the solution, which has been rendered alkaline with $(\text{H}_4\text{N})\text{OH}$.

Procedure when Subgroup B Alone is Present or when Subgroup A has been Removed.—Put into a small beaker the solution of the sulphides of subgroup B in yellow $(\text{H}_4\text{N})_2\text{S}_2$ and cautiously add diluted HCl until the solution is acid. If present arsenious sulphide, As_2S_3 , will be ppt. yellow; antimonous sulphide, Sb_2S_3 , orange-red, stannic sulphide, SnS_2 , yellow, Au_2S brown, PtS black. If only a white ppt. of sulphur appears the metals of subgroup B are absent.

Note.—Sn, whether present in the original solution in the stannous or in the stannic condition, will always appear at this point as stannic sulphide, SnS_2 , because both SnS and SnS_2 when dissolved in yellow $(\text{H}_2\text{N})_2\text{S}_2$ form the same compound.

If the ppt. is yellow or orange red, filter and wash it twice with hot water. If the presence of gold or platinum is suspected, dissolve the precipitate in hydrochloric acid containing a few crystals of potassium chlorate, evaporate to remove chlorine, then add KOH and boil, add some chloral hydrate to the solution and Au and Pt will be precipitated. Filter and wash with warm water, then dissolve ppt. in aqua regia (1 prt HNO_3 + 3 prts HCl), evaporate solution containing Au and Pt nearly to dryness, dilute with water, add to a portion of the solution stannous chloride containing a little stannic chloride, a purple ppt. confirms the presence of gold. To the balance of the solution containing Au and Pt add

(H_4N)OH until it is nearly neutral to test papers, then add (H_4N)Cl; if Pt is present it will be precipitated as black metallic platinum.

Return to the solution from which Au and Pt were precipitated with chloral hydrate, acidify with HCl and again pass H_2S through the solution, filter and wash twice with hot water.

Pour 10 c.c. of a concentrated solution of ammonic carbonate, (H_4N) $_2\text{CO}_3$, upon the ppt. As_2S_3 , if present, will be dissolved, in order to remove As_2S_3 completely, pass the solution through the paper several times. Put the solution into a small beaker and add conc. HNO_3 until it is acid. As_2S_3 , if present, will be ppt. If there is no ppt., As is absent. On the other hand, a ppt. must not be accepted as positive evidence of As.

Put the solution and ppt. into a small dish and evaporate to complete dryness under the hood. When the residue is cool, thoroughly mix it in a mortar with an equal quantity of a mixture consisting of sodic carbonate, Na_2CO_3 , and potassic nitrate, KNO_3 . Place some of the mixture upon a piece of platinum foil and with the iron pincers hold in the flame of the Bunsen burner until the mass fuses. Cool and place the platinum foil in a porcelain dish and add 10 c.c. of water, then place the dish on the iron gauze and heat to boiling. Cool and cautiously add a few drops of conc. HNO_3 until the solution is strongly acid. Remove the platinum foil from the liquid and add 5 c.c. of ammonic molybdate solution, heat gently; a yellow ppt. indicates the presence of As. Return to the residue insoluble in (H_4N) $_2\text{CO}_3$. Wash it once with hot water. Put some KClO_3 into a test-tube and add 5 c.c. of conc. HCl. Warm the solution and pour it upon the ppt. Collect it in another test-tube and pass it through the paper several times. It will dissolve Sb_2S_3 and SnS_2 . Dilute the solution with twice its volume of water and put it into a large beaker. Place some iron tacks into the solution and let stand for fifteen minutes under the hood. Sb will be deposited in the metallic condition as a black coating or residue and the Sn will remain in solution. Special

tests must be made for both metals. Filter and collect the filtrate in a test-tube. To confirm Sn, boil the filtrate for a few minutes then dilute with water until the volume is 20 c.c., and add a solution of HgCl_2 ; a white ppt. darkening upon standing indicates the presence of Sn.

To confirm the presence of Sb, wash the residue upon the paper several times with hot water then pour on the paper a solution of tartaric acid, $(\text{H}_2\text{C}_4\text{H}_4\text{O}_6)$, containing three drops of conc. HNO_3 . Evaporate the washings to almost dryness, cool and add water until the residue dissolves; add a few drops of conc. HCl and pass H_2S through the solution; an orange red indicates Sb.

GROUP III.

Introduction.—Seven metals are included under this heading, viz.: (1) Cobalt, Co; (2) Nickel, Ni; (3) Iron, Fe; (4) Aluminum, Al; (5) Chromium, Cr; (6) Manganese, Mn; (7) Zinc, Zn.

They are alike in their behavior toward ammoniac sulphide, $(\text{H}_4\text{N})_2\text{S}$, as they are precipitated by this reagent from a neutral or alkaline solution under these conditions excepting in the case of Al and Cr, which appear as hydroxides, sulphides are formed, viz.: (1) Co appears as black cobaltous sulphide, CoS . (2) Ni appears as black nickelous sulphide, NiS . (3) Fe appears as black ferrous sulphide, FeS . (4) Al appears as white gelatinous aluminic hydroxide, $\text{Al}(\text{OH})_3$. (5) Cr appears as gray-green gelatinous chromic hydroxide, $\text{Cr}(\text{OH})_3$. (6) Mn appears as flesh-colored manganous sulphide, MnS . (7) Zn appears as gray-white zinc sulphide, ZnS .

They may be identified by characteristic tests, viz.: (1) Co by blue bead with anhydrous borax, $\text{Na}_2\text{B}_4\text{O}_7$. (2) Ni by black ppt. $\text{Ni}(\text{OH})_3$. (3) Fe by testing original solution, viz.: (a) ferrous gives deep blue ppt. with $\text{K}_3\text{Fe}_2(\text{CN})_{12}$; (b) Ferric gives deep blue ppt. with $\text{K}_4\text{Fe}(\text{CN})_6$. (c) Ferric gives blood-red solution with KSCN . (4) Al by white,

gelatinous ppt. $\text{Al}(\text{OH})_3$. (5) Cr by yellow ppt. PbCrO_4 . (6) Mn by blue-green bead with Na_2CO_3 and KNO_3 . (7) Zn by gray-white ppt. ZnS from acetic acid solution.

Analytical Procedure.—Warm gently upon the iron plate in 500 c.c. flask, place the filtrate from the H_2S ppt. or a solution free from the bases of groups I and II. Add 10 c.c. of solution of ammoniac chloride, $(\text{H}_4\text{N})\text{Cl}$, next make the solution slightly alkaline with $(\text{H}_4\text{N})\text{OH}$, avoiding a large excess, as it interferes with the complete ppt. of Ni. If H_2S is in the solution $(\text{H}_4\text{N})\text{OH}$ will convert it into $(\text{H}_4\text{N})_2\text{S}$; as a result a black ppt. will appear if any metal having a black sulphide is present, also in the absence of H_2S the hydroxides of Fe, Cr, and Al will be ppt. by $(\text{H}_4\text{N})\text{OH}$ if these metals are present. Disregard any ppt. $(\text{H}_4\text{N})\text{OH}$ may cause. Finally add 10 c.c. of solution of ammoniac sulphide, $(\text{H}_4\text{N})_2\text{S}$. Cork the flask tightly and wrap a towel around it and shake vigorously for two minutes, filter a few cubic centimeters of the solution and add a drop of $(\text{H}_4\text{N})_2\text{S}$ to see if ppt. is complete. If it is not complete add 5 c.c. of $(\text{H}_4\text{N})_2\text{S}$. Cork, shake and test again. This should be repeated until ppt. is complete. All of the metals of group III will have been ppt. Filter into a small flask and keep the filtrate for group IV; make this filtration as quickly as possible and at the same time keep the ppt. from contact with air. Use a pleated filter and keep the funnel full with hot water to which a little $(\text{H}_4\text{N})_2\text{S}$ has been added. When the main part of the filtrate has been collected, set it aside and reject the wash water. Set the funnel holding the wash ppt. into a 250 c.c. flask, with a glass rod punch a hole through the paper and wash the ppt. into the flask with cold water. Cool thoroughly, add 10 c.c. of dilute HCl or enough to make the solution acid and shake well. Dilute HCl will dissolve everything except CoS and NiS . The color of the ppt. may give some indication as to what is present. A black ppt. shows that one or more of the metals having black sulphides is present. The black ppt., completely soluble in dilute HCl , shows that Fe is present and that Co and Ni are absent. A black ppt. incompletely soluble in dilute HCl shows positively that Co and Ni,

one or both, are present and that Fe may be. If it is not black, Co and Ni and Fe are absent. If dilute HCl does not completely dissolve the ppt., filter. Put the filtrate into a dish, add 5 c.c. of conc. HNO_3 and evaporate over the iron gauze to concentrate the solution and expel all H_2S .

The ppt. may contain CoS and NiS. Wash it well with hot water; make a perfectly clear bead of powdered borax, $\text{Na}_2\text{B}_4\text{O}_7$, on a small loop of platinum wire. Touch the bead to the ppt., taking care not to get too much on it, and fuse again until the bead is perfectly clear. Under these conditions both Co and Ni give colored beads. The Co bead is blue and will always mask the Ni bead which is reddish brown in the oxidizing, and gray in the reducing flame. If Co is absent the ppt. must be due to Ni. If Co is present a special test must be made for Ni, and it is generally advisable to make it anyway. Make, in a test-tube, a mixture of 6 c.c. of conc. HCl and 2 c.c. of conc. HNO_3 . Warm gently and pour it over the washed sulphide upon the paper, passing it through the paper several times CoS and NiS are dissolved. Pour the solution into a beaker and make it alkaline with NaOH; $\text{Co}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ are ppt.; filter, using paper of the smallest size and wash the ppt. with hot water; put 5 c.c. of water into a test-tube and make a strong solution of KCN. Set the funnel in a test-tube and pour the solution over the ppt., passing through the paper until everything is dissolved. KCN converts $\text{Ni}(\text{OH})_2$ into $\text{Ni}(\text{CN})_2\text{KCN}$, a double cyanide of Ni and K; $\text{Co}(\text{OH})_2$ into $\text{K}_6\text{Co}_2(\text{CN})_{12}$, potassic cobaltic cyanide. Add to the solution a few drops of NaOH and then bromine water in large excess. Co remains unchanged but Ni undergoes oxidation, which results in the formation of nickelic hydroxide, $\text{Ni}(\text{OH})_3$. This appears as a black ppt. or more frequently as a black ring at the zone of contact of the KCN solution with the bromine water. Heat sometimes facilitates the reaction. Return to the solution which has been evaporating in a dish, transfer it to a beaker, cool thoroughly and neutralize the acid with dry Na_2CO_3 . It is necessary that the solution be slightly acid. If a permanent ppt. is formed because too much Na_2CO_3 has been

used, cautiously add dilute HCl, drop by drop, until the ppt. is entirely dissolved. If the presence or absence of phosphates and oxalates has not been determined, this must now be settled before the next step is taken, as these substances interfere with the regular course of basic analyses.

Phosphates.—Mix 5 c.c. of the original solution with 5 c.c. of conc. HNO_3 and then add 10 c.c. of ammonic molybdate solution, $(\text{H}_4\text{N})_2\text{MoO}_4$; a yellow ppt. of phosphomolybdic acid appears in the cold. If the quantity of phosphate is small the ppt. forms upon standing.

Oxalates.—Add to 5 c.c. of the original solution enough dry Na_2CO_3 to render the solution strongly alkaline and boil for five minutes. Filter; acidify the filtrate with $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ and boil it to expel CO_2 . Cool and add a few drops of solution of calcic chloride, CaCl_2 . A white ppt. of calcic oxalate, CaC_2O_4 , will appear if oxalic acid is present.

Procedure when Phosphates and Oxalates are Absent.—Add to the nearly neutral solution 25 c.c. baric carbonate, BaCO_3 , suspended in water. Set aside for fifteen minutes and stir occasionally; BaCO_3 ppt. Fe, Al and Cr as hydroxide, but it has no action on Mn or Zn. Filter and keep the filtrate for the Mn and Zn tests.

The ppt. of the hydroxides of Fe, Al and Cr, together with the excess of BaCO_3 , must first be washed with hot water. Then set the funnel in a test-tube and pour dilute HCl over the ppt., passing it through the paper until everything is dissolved. Make the solution alkaline with $(\text{H}_4\text{N})\text{OH}$ which will ppt. the hydroxides of Fe, Al and Cr free from Ba. Filter, wash the ppt. with hot water and dry thoroughly without burning, by setting the paper in a funnel and pouring 5 c.c. of conc. HNO_3 over it, passing it through the paper until everything is dissolved. Add to the solution a few crystals of KClO_3 and warm gently; Cr, which is present in the basic condition as chromic nitrate, $\text{Cr}(\text{NO}_3)_3$, is oxidized and thereby converted into the acid condition as chromic anhydrite, CrO_3 . Cr in the basic condition gives green solutions. When the change has been brought about, the color should be reddish yellow. When oxidation is complete make the solu-

tion alkaline with NaOH. If Fe is present, it will appear as a reddish-brown ppt. of ferric hydroxide, $\text{Fe}(\text{OH})_3$.

Al will not appear as $\text{Al}(\text{OH})_3$, because in the presence of an excess of NaOH it is converted into sodic aluminate, $\text{Al}(\text{ONa})_3$, which is soluble in water. Cr in the acid condition is not ppt. by NaOH, but CrO_3 is converted into sodic chromate, Na_2CrO_4 , which is soluble in water. If there is a ppt. filter and ascertain by testing the original solution whether Fe is present in the ferrous or ferric condition. It is necessary to test the original solution, because processes of oxidation and reduction have been used in the analytical procedures as a result of which Fe is changed. Keep the filtrate for the Al and Cr tests. Two tests are available for Fe in the ferric and one for the ferrous conditions: Potassic ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, test for ferric iron; add to 5 c.c. of the original solution a few drops of dilute HCl and then a few drops of $\text{K}_4\text{Fe}(\text{CN})_6$. This reagent produces a light blue ppt. with ferrous Fe, but ferric compounds give a deep blue ppt. of "Prussian blue" or ferric ferrocyanide, $\text{Fe}_2(\text{Fe}(\text{CN})_6)_3$. It is necessary to discriminate between the two precipitates.

Potassic Sulphocyanate, KSCN, Test for Ferric Iron.—Add to 5 c.c. of the original solution a few drops of dilute HCl and then a few drops of KSCN or $(\text{H}_4\text{N})\text{SCN}$. Ferric Fe produces a deep blood-red coloration due to $\text{Fe}(\text{SCN})_3$.

Potassic Ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, Test for Ferrous Iron.—Add to 5 c.c. of the original solution a few drops of dilute HCl and then a few drops of $\text{K}_3\text{Fe}(\text{CN})_6$. This solution should be freshly prepared each time a test is made as it changes on standing.

Ferrous FeS, produces a deep blue ppt. of "Turnbull Blue" or ferrous ferricyanide, $\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$.

Divide into two equal portions the filtrate which may contain Al and Cr, add to one portion twice its volume of $(\text{H}_4\text{N})\text{Cl}$, and heat to boiling. Al if present will appear as a white gelatinous ppt. or $\text{Al}(\text{OH})_3$; render the second portion acid with $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ and then add a few drops of a solution of plumbic acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. Cr if present will appear as yellow ppt. plumbic chromate, PbCrO_4 .

Return to the filtrate which may contain Mn and Zn. Pour it into a beaker and heat nearly to boiling on the iron plate. Stir and add dilute H_2SO_4 until a drop ceases to cause a white ppt. The object of this step is to free the solution from Ba which came from the BaCO_3 that caused the ppt. of Fe, Al, and Cr. Filter to remove BaSO_4 , render the filtrate alkaline with NaOH and boil five minutes. Mn if present will be precipitated as flocculent, flesh-colored, manganous hydroxide, $\text{Mn}(\text{OH})_2$. Upon standing, especially if exposed to the air, $\text{Mn}(\text{OH})_2$ undergoes oxidation and the color changes to brown owing to the formation of manganic oxyhydroxide, $\text{Mn}_2\text{O}_2(\text{OH})_2$. Zn, on the other hand, is not ppt. because $\text{Zn}(\text{OH})_2$ in the presence of an excess of NaOH is converted into sodic zincate, $\text{Zn}(\text{ONa})_2$, which is soluble in water. Filter and wash the ppt. The fact that NaOH produces a ppt. must not be accepted as final proof of Mn, but a special test for it should be made. Touch a heated loop to a little fusion mixture composed of equal parts of Na_2CO_3 and KNO_3 , then heat in the blow-pipe flame for an instant to cause the salts to adhere to the wire. Touch the salt to the ppt. and fuse until bubbles of gas no longer appear. Mn if present will give an opaque blue-green bead owing to the formation of sodic manganate, Na_2MnO_4 .

Add to the filtrate, which may contain Zn, enough $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ to render the solution acid. $\text{Zn}(\text{ONa})_2$ will change to zincic acetate, $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$.

Pass H_2S through the solution until it smells strongly of the gas. Zn if present will appear as a gray-white ppt. of zincic sulphide, ZnS . Sometimes the ppt. becomes apparent only on long standing.

Procedure when the Phosphates or Oxalates are Present.—At first sight it is not apparent why the presence of phosphates or oxalates should occasion a change in the course of analysis; it is due to the fact that they cause certain metals properly belonging elsewhere to be ppt. along with the metals of group III.

The ppt. of the metals of group III takes place in an alkaline solution. Under these conditions phosphates or

oxalates of Ba, Sr, Ca and Mg are also ppt. since they are soluble only in an acid solution. Therefore, if a solution under examination contains phosphates or oxalates and at the same time Ba, Sr, Ca, or Mg, these metals will be ppt. in group III along with the regular members of the group and the course of analysis must be modified in such a way as to admit of their detection in this place.

Add to a small portion of the filtrate, which has been evaporated with conc. HNO_3 , dil. H_2SO_4 . If no ppt. appears after five minutes' standing, Ba and Sr are absent. If there is a ppt., filter and wash it thoroughly with hot water. It may consist of the sulphates of Ba and Sr. It is best examined for Ba and Sr in the spectroscope, the presence of the former being recognized by four green bands and the latter by one orange, two red, and one blue band. To test for Ca, take either the solution found free from Ba and Sr, or the filtrate from the ppt., caused by these two metals and add to it three times its volume of alcohol; CaSO_4 , being less soluble in a mixture of alcohol and water than it is in water, will ppt. if Ca is present. To confirm the presence of Ca filter and dissolve the ppt. in a little hot water.

The addition of a solution of ammonic oxalate, $(\text{H}_4\text{N})_2\text{C}_2\text{O}_4$, will produce a white ppt. of calcic oxalate, CaC_2O_4 . Having completed the test for Ba, Sr and Ca, return to the main portion of the filtrate which was evaporated with conc. HNO_3 . Nearly neutralize the free acid with dry Na_2CO_3 , taking care to have no permanent ppt.

Then add to it solution of ferric chloride, FeCl_3 , until a drop of the solution placed upon a watch-glass gives a yellow ppt. when made alkaline with a drop of $(\text{H}_4\text{N})\text{OH}$. FeCl_3 is added because Fe will combine with H_3PO_4 and $\text{H}_2\text{C}_2\text{O}_4$ and thus prevent the alkali earth metal from being ppt. as phosphates and oxalates at the next step in the analysis. Add to the solution 25 c.c. of BaCO_3 suspended in water, stir occasionally and let stand ten minutes. It will be well to consider what metals will be ppt. at this point, and what remains in solution. The ppt. produced by BaCO_3 is not essentially different from the ppt. produced by the same reagent when

the phosphates and oxalates are absent. It may contain Al, as $\text{Al}(\text{OH})_3$ and Cr as $\text{Cr}(\text{OH})_3$; it must contain Fe combined with H_3PO_4 or $\text{H}_2\text{C}_2\text{O}_4$ and the excess of BaCO_3 . Examine it precisely as before and test the original solution for Fe, remembering a ppt. appearing at this point means nothing, since FeCl_3 was added above as a reagent. The filtrate from the BaCO_3 ppt. may contain Mn, Zn, Sr, Ca, and Mg; it must contain Ba. Heat on the iron plate nearly to boiling and add dil. H_2SO_4 until a drop ceases to cause a ppt. Ba and Sr will be ppt. Filter, make the filtrate alkaline with $(\text{H}_4\text{N})\text{OH}$ and add $(\text{H}_4\text{N})_2\text{S}$. If there is no ppt. Mn and Zn are absent. A ppt. means Mn and Zn, one or both. Filter and wash the ppt. with hot water. Then dissolve it in cold dil. HCl . Render the solution alkaline with NaOH and heat nearly to boiling on the iron plate. If there is no ppt., Mn is absent. If there is a ppt., filter, wash and examine as before for Mn with Na_2CO_3 and KNO_3 bead. The filtrate from the ppt. which may contain Mn is acidified with $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ and then saturated with H_2S . Zn if present will be ppt. as gray-white ZnS . The filtrate from the ppt. caused by $(\text{H}_4\text{N})_2\text{S}$ or the solution found not to contain Mn or Zn is treated with ammoniac oxalate, $(\text{H}_4\text{N})\text{C}_2\text{O}_4$. A white ppt. is CaC_2O_4 due to the presence of Ca; filter and add sodic phosphate, Na_2HPO_4 , to the filtrate. If Mg is present it will be ppt. as white crystalline ammoniac magnesian phosphate, $\text{Mg}(\text{H}_4\text{N})\text{PO}_4$.

GROUP IV.

Introductory.—Four metals are included under this heading, viz.: (1) Barium, Ba; (2) Strontium, Sr; (3) Calcium, Ca; (4) Magnesium, Mg. With the exception of Mg these metals are alike in their behavior toward ammoniac carbonate, $(\text{H}_4\text{N})_2\text{CO}_3$, as they are ppt. by this reagent from a neutral or alkaline solution. Under these conditions Mg is not ppt. at all but the other members of the group form carbonates, viz.:

1. Ba appears as white baric carbonate, BaCO_3 .
2. Sr appears as white strontic carbonate, SrCO_3 .

3. Ca appears as white calcic carbonate, CaCO_3 .

4. Mg remains in solution.

They may be identified by characteristic tests:

1. Ba by insoluble white, BaSO_4 , appearing immediately.

2. Sr by insoluble white, SrSO_4 , appearing tardily.

3. Ca by insoluble white, CaC_2O_4 .

4. Mg by insoluble white crystalline, $\text{Mg}(\text{H}_4\text{N})\text{PO}_4$.

Analytical Procedure.—Add to the filtrate from the $(\text{H}_4\text{N})_2\text{S}$ ppt. of group III, or to a solution free from the metals of groups I, II, III, 10 c.c. of $(\text{H}_4\text{N})\text{Cl}$, provided this reagent is not already present.

Note.—After the addition of $(\text{H}_4\text{N})\text{Cl}$ the solution is made alkaline with $(\text{H}_4\text{N})\text{OH}$. If the solution contains Mg and $(\text{H}_4\text{N})\text{Cl}$ is not present the addition of $(\text{H}_4\text{N})\text{OH}$ will cause the partial ppt. of Mg as $\text{Mg}(\text{OH})_2$ and this metal may escape detection. Soluble compounds of Mg form double salts with $(\text{H}_4\text{N})\text{Cl}$ and upon them $(\text{H}_4\text{N})\text{OH}$ has no action. It is for this reason that $(\text{H}_4\text{N})\text{Cl}$ is used at this point as well as in group III. If the solution is not alkaline, make it so by adding a slight excess of $(\text{H}_4\text{N})\text{OH}$. Heat nearly to boiling on the iron plate and add ammonic carbonate, $(\text{H}_4\text{N})_2\text{CO}_3$, until a drop ceases to cause a ppt.

If you are dealing with a much diluted filtrate from group III, it may be advisable to concentrate it by evaporation before making this precipitation. When ppt. is complete, set aside for a few minutes and then filter. The filtrate may contain Mg together with the members of group V. Add to a small portion of the filtrate a few drops of a solution of sodic phosphate, Na_2HPO_4 . If Mg is present an insoluble white crystalline ppt. of ammonic magnesian phosphate, $(\text{H}_4\text{N})\text{-MgPO}_4$ will appear. If the quantity of Mg is small it may be necessary to let the solution stand for some time. The precipitate should be examined with a lens to make sure that it is crystalline because, in case of incomplete ppt. by $(\text{H}_4\text{N})_2\text{-CO}_3$, some Ba, Sr, or Ca might pass into this filtrate. Na_2HPO_4 ppt. these metals also from solution but the compounds are amorphous. Having tested for Mg, keep the remainder of the filtrate for the group V tests. The pre-

precipitate, which may consist of BaCO_3 , SrCO_3 and CaCO_3 , is first thoroughly washed with hot water. It is then dissolved on the paper with acetic acid, $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$. The carbonates are decomposed and converted into acetates. To a small portion of the solution add a few drops of solution CaSO_4 . Three cases may arise, viz.: (1) A white ppt. may appear immediately. It will be BaSO_4 , and Ba is present. Sr and Ca also may be present. (2) A white ppt. may appear tardily. It will be SrSO_4 , and Sr is present. Ba must be absent but Ca also may be present. (3) There may be no ppt. at all. Then Ba and Sr are absent, Ca alone is present and the original ppt. is CaCO_3 .

The subsequent course of analysis depends upon the case which arises and it must be modified accordingly. If Ba is present it must be removed from solution before testing for Sr and Ca can be made. Add solution of potassic chromate, K_2CrO_4 , in slight excess to the remainder of the $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ solution. Ba will be ppt. as Ba chromate, BaCrO_4 , but Sr and Ca will remain in solution. Filter and make the filtrate alkaline with $(\text{H}_4\text{N})\text{OH}$. A sufficiency of the reagent will change the color from red to yellow. Heat nearly to boiling on the iron plate and as before add $(\text{H}_4\text{N})_2\text{CO}_3$ until a drop ceases to cause a precipitate. If there is no ppt., Sr and Ca are absent and the original ppt. must have consisted of BaCO_3 alone. If a ppt. appears, filter after a few minutes' standing and reject the filtrate. The ppt. which may consist of SrCO_3 and CaCO_3 , one or both, must be washed with hot water until all traces of yellow color is removed. It is then dissolved on the paper in $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$. Again the carbonates have been converted into acetates. Add a few drops of solution of CaSO_4 to a small portion of the acetate solution. Two cases may arise, viz.: (1) A white ppt. may appear tardily. It would be SrSO_4 , and Sr is present; Ca may also be present. (2) There may be no ppt. at all. Then Sr is absent and the precipitate caused the second time by $(\text{H}_4\text{N})_2\text{CO}_3$ must have consisted of CaCO_3 alone. If Sr is present it must be removed before testing for Ca. Add dil. H_2SO_4 in slight excess to the remainder of the $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ solution, from

which Ba has been removed or in which Ba was originally found absent.

Note.—Observe that in case Ba is shown to be absent when the test is made with CaSO_4 in the first $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ solution of the carbonates, and Sr is present, the analysis continues from the paragraph beginning “If Sr is present, etc.”

If Sr is also shown to be absent, then it continues from the paragraph below beginning, “If Sr is absent, etc.”

As SrSO_4 separates slowly, do not proceed hastily, but allow the solution to stand about fifteen minutes. If Ca is present in large quantity, or the solution is concentrated, some CaSO_4 will also be ppt. with SrSO_4 , but this may be disregarded.

Filter and make the filtrate alkaline with $(\text{H}_4\text{N})\text{OH}$. Then add solution of ammonic oxalate, $(\text{H}_4\text{N})_2\text{C}_2\text{O}_4$. If Ca is present, a white ppt. of calcic oxalate, CaC_2O_4 , will appear. If Sr is absent whether Ba was originally absent or was removed $(\text{H}_4\text{N})\text{OH}$ and $(\text{H}_4\text{N})_2\text{C}_2\text{O}_4$ added to the rest of the $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ solution precipitates CaC_2O_4 , if Ca is present.

GROUP V.

Introductory.—Four metals are included under this heading, viz.: (1) Ammonium, (H_4N) ; (2) Sodium, Na; (3) Potassium, K; (4) Lithium, Li. These metals differ from those of the preceding groups in having no general reagent which can be used to precipitate them from solution. This is because their compounds with few exceptions are readily soluble in water. Therefore they remain in solution after the other metals have been precipitated and tests have to be used by which each can be detected in presence of the others. Ammonium, (H_4N) —this substance is hypothetical and exists only in combination with other elements. It is placed in this group because its compound closely resembles in properties those of the alkali metals. In testing for it, it is necessary to show that ammonic, H_3N , can be obtained from the solution, or a substance under examination. In the case of a solution

which has passed through the course of basic analysis a test for ammonium evidently cannot be made at the end of the analysis, because ammonium salts have several times been used as reagents and they must be in the solution. Some of the original material must always be used in testing for this substance.

Ammonium Test.—Select a tall beaker and have it clean. Place some dry calcic hydroxide, Ca(OH)_2 , in the bottom, but do not get it on the sides. Add a little of the original solution or solid dissolved in water and H_3N will be set free if salts of (H_4N) are present. Often H_3N may be detected by its odor, but it is better to place a piece of moistened turmeric paper on the outside of a clean dish and set it on the beaker if a test for (H_4N) is not obtained in the cold; warm gently on the iron plate. Avoid spattering, since Ca(OH)_2 also has the same effect upon turmeric paper.

Tests for the three remaining members of this group must be made with the filtrate of group IV. Owing to the fact that this filtrate may contain Mg also, two cases arise, viz.:

1. When Mg has been shown to be present, Mg must be removed from solution before the remaining test of this group can be made. Pour the solution into a dish and evaporate under the hood over wire gauze to complete dryness, and continue the heating until all fuming has ceased. To insure good results directions must be followed carefully. The object of this step is the complete removal of (H_4N) salts, as they interfere with the removal of Mg. When heat expels nothing more, allow the dish to cool and dissolve the residue in 5 c.c. of water. Add 5 c.c. of solution of baric hydroxide, Ba(OH)_2 , or enough to give an alkaline reaction. Mg will be completely precipitated as magnesian hydroxide, Mg(OH)_2 . Filter and heat the filtrate on the iron plate nearly to boiling. The excess of Ba(OH)_2 must now be removed. Add dil. H_2SO_4 until a drop ceases to cause a ppt. and filter. Again evaporate the filtrate under the hood and heat until everything volatile has been expelled, cool and dissolve the residue in 5 c.c. of water. Na, K and Li if present will now be in solution as NaHSO_4 , KHSO_4 and LiHSO_4 ;

the acid sulphate and this solution after being filtered into a clean specimen tube may be used for the flame test to be described later.

2. When Mg has been shown to be absent, as already described, the filtrate from group IV must be evaporated until fuming has entirely ceased. The cooled residue is dissolved in 5 c.c. of water, and the solution filtered into a clean specimen tube for use in the flame tests.

In the absence of a spectroscope the flame tests may be observed through one or more pieces of cobalt glass. Dip a platinum wire into the filtrate from the specimen tube and hold wire in the colorless flame of a Bunsen burner.

The Na light is absorbed by passing through the cobalt glass and the flame will thus appear colorless. In viewing the sodium flame without the use of the cobalt glass it has a yellow color. The potassium flame appears violet, and through the cobalt glass more of a crimson; in this way Na and K may both be detected. However, Li appears crimson in the flame and also crimson through the cobalt glass, resembling the K flame. Li and K cannot be distinguished from each other by using the cobalt glass. In this case it will be necessary to use a spectroscope.

CHAPTER XXVII.

ELECTROMETALLURGY.

WHEN an electric current is passed through a solution of a salt of a metal, decomposition takes place and the metal is precipitated from solution. Depending upon the conditions under which the metal has been precipitated, it may be obtained in powder form or as a coherent mass.

The process of so precipitating metals is called electro-metallurgy.

There are two different methods in use in electrometallurgy.

1. The metal is deposited in a mold until a desired thickness has been obtained. This process is known as electrotyping or galvanoplastics.
2. Depositing the metal upon a metallic surface as a thin, coherent coating. This process is known as electroplating.

ELECTROTYPING.

In this process a mold is first prepared. This process has been used in dentistry for the construction of a gold base for the attachment of artificial teeth. This process has not proved successful in dentistry; however, it will serve to illustrate this method of depositing metals with an electric current.


The plaster model is carefully prepared and thoroughly dried, it is then boiled in paraffin so as to make it impervious to the solution of the bath. The surfaces to receive the metallic deposit is then coated with a thin layer of graphite, care being taken not to efface the fine lines of the model. Graphite is used so as to form a conducting surface upon the model. The model is then connected in metallic circuit with the

negative pole of a battery, the positive pole is connected with a strip of metal having at least the same surface area as the model. If the metal to be deposited is gold, then a sheet of gold having at least the same area as the model should be used.

The bath is composed of a nearly neutral solution of gold chloride in potassium cyanide. The nature of the gold deposited is dependent upon the density of the current; with a current of moderate density the gold will be deposited as a crystalline mass but with a greater density of the current it will be thrown down as a non-coherent mass.

As the current passes from the positive electrode (gold sheet) the charge is conveyed by the gold ions in the solution to the negative electrode (the model), the gold ions here lose the electrical charge and the gold is deposited upon the model. While this change is taking place the cyanogen ions, which possess a negative charge, are passing in an opposite direction and upon coming in contact with the anode (gold sheet) lose their charge and attack the gold, in this manner the bath is kept of a constant concentration as to the gold which is in solution. In the case which is illustrated the gold piece of the anode should exceed in weight the metallic base which is desired.

ELECTROPLATING. ELECTROGILDING.

In order to deposit a thin film of gold upon the surface of a metal a preliminary preparation of the surface is necessary: (1) The object must be freed from any fatty material. This may be accomplished either by heating and then removing any oxides which may be found by the use of dilute nitric acid, finally washing thoroughly with distilled water. In this operation the piece should not come in contact with the hands of the operator or the piece will be contaminated by the grease from the hands. (2) The piece may be heated in a solution of sodium carbonate and in this way remove the grease. After this treatment a thorough washing is necessary to remove an adhering sodium carbonate solution. 

After the piece has been freed from grease its surface should be thoroughly brushed with a hard brush, washed in distilled water and dried in gently heated sawdust. Connect the piece with the negative pole from a battery and have a piece of gold of at least the same surface area as the piece to be plated.

The gold bath may be prepared by having one part auric chloride, (AuCl_3), ten parts potassium cyanide and two hundred parts distilled water. The density of the current should not exceed 0.8 ampère per square decimeter of the surface of the piece to be plated.

Silver, copper, and German silver may be gilded, while iron, steel, zinc, tin and lead are very difficult to plate. Some metals take a much better plating if they are first copper plated. The color of the gold plating may be attained by adding small quantities of silver or copper to the bath.

Electrosilvering.—This process may be carried out in the same manner as the above except the anode must be of silver and also a silver bath must be used.

SILVER BATH.

Silver cyanide	2 parts
Potassium cyanide	2 parts
Water	250 parts

The density of the current should be 0.33 ampère per square decimeter of the surface of the cathode.

Nickel Plating.—The following is said to produce a good nickel plating:

Preparation of Bath.—Dissolve one part of nickel ammonium sulphate in ten parts by weight of water. The nickel ammonium sulphate should be free from alkaline oxide and other impurities. After the solution is prepared, filter. The anode should be of nickel, using the same size electrode as specified above under Gold Plating. One difficulty in nickel plating is that the metal is not always uniformly deposited and may scale from the piece. To overcome this difficulty the object should be removed from the bath frequently and

polished, then replace until a sufficiently heavy plating of nickel is obtained.

Platinum plating is effected by dissolving platinum hydrate in syrupy phosphoric acid and this solution diluted with water until it contains 1.2 to 1.5 per cent. of the hydrate. The anode is either of carbon or platinum and the strength of the bath is kept constant by the addition of the hydrate.

Objects of iron, nickel and zinc must first be copper plated before they can receive a deposit of gold, silver or platinum.

Contact Process.—In this process a strip or rod of an electro-positive metal is brought in contact with the object to be plated when the latter is immersed in a bath containing a salt of the metal to be deposited; for example, a plate of zinc in a bath of gold cyanide. When the zinc touches the object a battery is formed, zinc being the anode and the object the kathode, and the gold cyanide the electrolyte; the solution is decomposed and gold is deposited upon the object.

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